KOSSOWSKI, Stanislaw; GIELDANOWSKI, Jerzy; ZIEMSKI, Zbigniew

Senile deafness and the use of vitamin preparations. Otolaryng.
Pol. 18 no.3:335-340 '64

1. Z Kliniki Otolaryngologicznej Akademii Medycznej we Wroclawiu
(Kierownik: prof. dr. W. Jankowski) i z Zakladu Farmakologii
Akademii Medycznej we Wroclawiu (Kierownik: prof. dr. J. Hano).

KOSSOWSKI, Stanislaw; AGOPSOWICZ, Grzegorz; CYRULEWSKA, Jadwiga

Use of Polyester fabrics in Eyries' operation. Otolaryng. Pol. 18 no.3:433-434 '64

1. Z Kliniki Otolaryngologicznej Akademii Medycznej we Wroclawiu. (Kierownik: prof. dr. W. Jankowski).

KOSSOWSKI, Stanislaw; GIELDANOWSKI, Jerzy; ZIEMSKI, Zbigniew

Aging of the organ of hearing according to the Wroclaw modification of Feldmann's test. Otolaryng. Pol. 18 no.1:39-46 '64.

1. Z Kliniki Otolaryngologicznej Akademii Medycznej we Wroclawiu (Kierownik: prof. dr W. Jankowski) i z Zakladu Farmakologii Akademii Medycznej we Wroclawiu (Kierownik: prof. dr J. Hano).

KOSSOWSKI, S.; AGOPSOWICZ, G.

The importance of the antibiogram in diseases caused by Klebsiella. Cesk. otolaryng. 14 no.1:40-44 F'65.

1. Otolaryngologicka klinika A.M. ve Wroclawi (prednosta: prof. dr. W. Jankowski).

KOSSOWSKI, Stanislaw; GIELDANOWSKI, Jerzy; ZIEMSKI, Zbigniew

Audiometric localization of injuries of the central auditory tracts. Otolaryng. Pol. 19 no.2:163-168 '65.

1. Z Kliniki Otolaryngologicznej Akademii Medycznej we Wroclawiu (Kierownik: prof. dr. W. Jankowski) i z Zakladu Farmakologii Akademii Medycznej we Wroclawiu (Kierownik: prof. dr. J. Hano).

PLOCIENNIK, Zygmunt, inz.; KOSSOWSKI, Wladyslaw, inz.

Transportable apparatus for testing and controlling installations of central heating during the summer. Gosp paliw 11 Special issue no.(95):5-8 Ja '63.

1. Ministerstwo Gospodarki Komunalnej, Wydzial Cieplownictwa, Warszawa (for Plociennik). 2. Miejskie Przedsiebiorstwo Instalacyjne, Warszawa (for Kossowski).

WOJEWSKI, Alfons; KOSSOWSKI, Wojciech

Experimental urinary calculi. Pol. tyg. lek. 18 no.46:1717-1720 11 N'63

1. Z Kliniki Urologicznej PAM w Szczecinie; kierownik: doc. dr. A. Wojewski.

KOSSOY, A.

Nature and role of cooperation during the period of the transition from capitalism to socialism. Vop. ekon. no.2:82-92 F '63. (MIRA 16:3)

(Cooperation)

KOSSOY, A.

Is it a proper way to interpret important theoretic problems? ("Main problems of the political economy of socialism in V.I. Lenin's work by N.D. Kolesov and others. Reviewed by A. Kossoi). Vop. ekon. no.8:142-146 Ag '61. (MIRA 14:7)

(Economics) (Lenin, Vladimir Il'ich, 1870-1924)
(Kolesov, N.D.) (Grigor"ev, P.G.) (Feshekhonov, V.A.)
(Pliner, M.D.) (Raud, V.M.) (Fedorova, L.P.)
(TSelykovskaia, E.A.)

GLADKOV, I.A., doktor ekon.nauk; KOSSOY, A.I., kand.ekon.nauk; GORBUNOV, E.P., nauchnyy sotrudnik; YAKOVTSEVSKIY, V.N., kand.ekon.nauk; ORLOV, B.P., kand.ekon.nauk; DIKHTYAR, G.A., kand.ekon.nauk; D'YACHENKO, V.P.; PAVLOV, K.P., kand.ekon.nauk; CHEBOTAREV, V.A., nauchnyy sotrudnik; BAKOVETSKAYA, V.S., red.izd-va; GOLUB', S.P., tekhn.red.

[The Soviet national economy, 1921-1925] Sovetskoe narodnoe khoziaistvo v 1921-1925 gg. Moskva, 1960. 558 p. (MIRA 13:3)

1. Akademiya nauk SSSR. Institut ekonomiki. 2. Chlen-korrespondent AN SSSR (for D'yachenko).
(Russia--Economic conditions)

GLADKOV, I.A., doktor ekon. nauk; KOSSOY, A.I., kand. ekon. nauk; VIDONOV, S.S., nauchn. sotr.; SAMOYLOVA, I.D., nauchn. sotr.; GORBUNOV, E.P., kand. ekon. nauk; MAYEVSKIY, I.V., doktor ekonom. nauk;CHEBOTAREV,V.A., kand. ekon. nauk; KAMUSHER, L.N., nauchn. sotr.; STROYEVA, Z.N., nauchn. sotr.; FOMINA, L.V., nauchn. sotr.; VOROB'YEV, Yu.F., kand. ekon. nauk; KRAYEV, M.A., doktor ekon. nauk; KAPLINSKIY, Ye.M., kand. ekon. nauk; LAPINA, S.N., nauchn. sotr.; YAKOVTSEVSKIY, V.N., kand. ekon. nauk; ORLOV, B.P., kand. ekon. nauk; DIKHTYAR, G.A., doktor ekon. nauk [deceased]; PLOTNIKOV, K.N.; MALIKOVA, A.I., nauchn. sotr.; TOVMOSYAN, M.Ye., red.izd-va; POLYAKOVA, T.V., tekhn. red.

[Socialist national economy of the U.S.S.R. in 1933 to 1940] Sotsialisticheskoe narodnoe khoziaistvo SSSR v 1933-1940 gg. Moskva, Izd-vo AN SSSR, 1963. 665 p. (MIRA 16:12)

1. Akademiya nauk SSSR. Institut ekonomiki. 2. Sektor istorii narodnogo khozyaystva Instituta ekonomiki AN SSSR (for Stroyeva,Fomina, Kaplinskiy, Lapina). 3. Chlen-korrespondent AN SSSR (for Plotnikov).

(Russia—Economic conditions)

KOSSOY, A.I.

"Problems of state capitalism during the transition period from capitalism to socialism" by A.G.Seid-Guseinov; " State capitalism in the U.S.S.R. during the transition period from capitalism to socialism" by I.D.Brin. Reviewed by A.Kossoi. Vop. ekon. no.12: 121-130 D '60. (MIRA 13:12)

(Communist countries--Economic policy)

(Brin, I.D.)

KOSSOY, A. S.

USSR/Chemical Technology - Chemical Products and Their Application. Wood Chemistry
Products. Cellulose and Its Manufacture. Paper, I-23

Abst Journal: Referat Zhur - Khimiya, No 19, 1956, 63369

Author: Kossoy, A. S.

Institution: None

Title: Water Hydrolysis of Wood as the Preliminary Stage of Sulfate Cooking of Birch Wood Viscose Cellulose

Original Periodical: Tr. Leningr. tekhnol. in-ta im. V. M. Molotova, 1955, No 3, 44-53

Abstract: As optimal conditions of preliminary hydrolysis which ensure maximum preservation of cellulose (C) with concomitant passing into solution of greatest possible amount of hemicelluloses (HC), is recommended a treatment of chips with water at 180° for 15-30 minutes. On such a treatment more than 13% of pentosan (P) are removed, while losses of C amount to 3.6% of the weight of the wood. Bleached C obtained after preliminary hydrolysis contains (in %): α-cellulose 94.5-94.7, P 3.6-4.14, lignin 0.35-0.38, ash 0.16-0.30; yield of bleached C

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USSR/
Products. Cellulose and Its Manufacture. Paper, I-23

Abst Journal: Referat Zhur - Khimiya, No 19, 1956, 63369

Abstract: 33.2-33.5%. After additional inversion the hydrolyzate contains ~15% HC on the basis of initial wood or ~0.45 t per one t of C, and can be used for the production of food or feed yeast.

Card 2/2

KOSSOY, A.S., kand. tekhn. nauk

Chemical woodpulp for newsprint and hanging paper. Bum. prom. 37 no.7:3-7 Jl'62. (MIRA 17:2)

1. Leningradskiy tekhnologicheskiy institut tsellyulozno-bumazhnoy promyshlennosti.

KOSSOY, A.S., kand.tekhn.nauk, dots.

[redacted] Chemical pulp from wood chips. Bum.prom. 33 no.10:6-9 O '58.
(MIRA 11:11)

1. Leningradskiy tekhnologicheskiy institut.
(Woodpulp)

GUBERNSKAYA, L.T., red.; KOSSOY, A.S., red.; EYDLIN, I.Ya.,
red.; YAKUBOVICH, S.Z., red.

[New developments in woodpulp and paper production; from reports delivered by British and American experts on January 26 1962 in the State Committee of the Council of Ministers of the U.S.S.R. on Research Coordination] Novoe v tselliulozno-bumazhnom proizvodstve; po dokladam angliiskikh i amerikanskikh spetsialistov 26 ianvaria 1962 g. v Gosudarstvennom komitete Sovete Ministrov SSSR po koordinatsii nauchno-issledovatel'skikh rabot. Moskva, 1962. 89 p. (MIRA 17:9)

1. Moscow. TSentral'nyy institut tekhnicheskoy informatsii i ekonomicheskikh issledovaniy po lesnoy, bumazhnoy i derevoobrabatyvayushchey promyshlennosti.

KOSSOY, A.S., kand.tekhn.nauk

Use of lumbering wastes for the manufacture of fibrous semi-finished products. Bum.prom. 38 no.1:29-30 Ja '63.
(MIRA 16:2)

1. Leningradskiy tekhnologicheskiy institut tsellyulozno-bumazhnoy promyshlennosti.
(Woodpulp) (Lumbering)

KOSSOY, B. S.

④

Equipment of Glass Plants (Oborudovanie stekol'nykh zavodov), K. I. Veinberg, B. S. Kossoi, M. P. Vol'ken, and M. I. Reznikov. Promstroiizdat, 1952. Price 19 rubles. Reviewed in *Steklo i Keram.*, 10 [2] 27–29 (1953).—The book covers equipment, its operation, organization of preventive maintenance, lubrication, and repair. B.Z.K.

BREKHOVSKIKH, S.M.[reviewer]; VEYNBERG, K.L.; KOSSOY, B.S.; NOL'KEN, M.P.;
REZNIKOV, M.I. [authors].

Useful manual ("Glass manufacturing plant equipment." K.L.Veinberg, B.S.Kossoi, M.P.Nol'ken, M.I.Reznikov. Reviewed by S.M.Brekhovskikh). Stek.i ker. 10 no.12:27-29 D '53. (MLRA 6:11)
(Glass manufacture) (Veinberg, K.L.) (Kossoi, B.S.)

VEYNBERG, K.L.; KOSSOY, B.S.; NOL'KEN, M.P.; REZNIKOV, M.I.; KADANER, N.I., red. izd-va; RUDAKOVA, N.I., tekhn. red.

[Equipment for glass plants] Oborudovanie stekol'nykh zavodov. Pod red. M.I.Reznikova. Izd.2., ispr. i dop. Moskva, Gos. izd-vo lit-ry po stroit., arkhit. i stroit. materialam, 1961. 618 p. (MIRA 14:8)

(Glass manufacture—Equipment and supplies)

KOSSOY, M. S.

Technology

Residual stresses and cyclical strength of construction steel during surface induction hardening, (Moskva?), Mashgiz, 1951.

Monthly List of Russian Accessions, Library of Congress, October 195[illegible]. Unclassified.

S/114/61/000/003/001/002
E194/E235

AUTHOR: Kossoy, M. S., Engineer

TITLE: Experience of Introducing the Process of Electrical Heat Treatment of Welded Joints on Steam Piping in the Cherepet' GRES

PERIODICAL: Energomashinostroyeniye, 1961, No. 3, pp. 28-31

TEXT: In 1958 TsNIITMASh developed a process for the high-temperature austenization of welds on steam piping under erection and repair conditions using induction heating at a frequency of 2 500 c/s. The new process has considerable advantages over heating with electrical muffle furnaces and the even heating that it produced gave very good metallurgical results. The investigation also showed that power frequency a.c. has advantages for pipe weld heating as no special high-frequency convertor is required and the welds may be heated by solenoid type inductors operating at 220 or 370 V. The high frequency portable equipment that was used in the Cherepet' GRES is then described. It was based on the packaged heating equipment Type МГЗ-102 (MGZ-102) of the Elektropech' Trust and consists of a frequency changer, a control

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Experience of Introducing the Process of Electrical Heat Treatment of Welded Joints on Steam Piping in the Cherepet' GRES

kiosk and control panel, a flexible inductor cable and appropriate extension cables. The frequency changer is Type ПВС-100/2500-1 (PVS-100/2500-1) with an output of 100 kW and frequency of 2500 c/s. A number of base plates are provided at different places in the station on which the frequency changer can be installed. The flexible conductor is built up of two cores of bare copper wires grade МГГ (MGG) of 150 mm^2 cross section contained in a standard linen fire hose of 51 mm diameter. The inductor is 7.5 m long. The conductors are clipped together at intervals of about 650 mm. The extension cables are of similar construction but use rubberized hose. They are used to connect the inductors to the control panel when this cannot be put alongside the job. Heat insulation consisting of sheet asbestos 15-20 mm thick is wrapped round the joint to be heated and the inductor is wound on this. The inductor and extension cables are water-cooled. Numerous minor design features of the equipment are described. Heat treatment was first tried on welds in main pipework in the Turbine room. The internal diameter

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Experience of Introducing the Process of Electrical Heat Treatment of Welded Joints on Steam Piping in the Cherepet' GRES

of the pipes was 27 mm and the external 219 mm, the grade of steel was 1X18H12T (1Kh18N12T), the heating temperature was 1 075 ± 25°C, the mean rate of heating was 20-22°C per minute, the welds were maintained at the maximum temperature for one hour and were then cooled at an average rate of 6-7°C per minute. Six turns of the inductor were wound round the weld. The weld temperature was checked with a thermo-couple. The power consumption was 75-80 kW during the heating period and maximum temperature was maintained with an output of 40-45 kW. Immediately after heat treatment the welds were inspected and found satisfactory. During erection of the main pipework of one boiler 75 welded joints were treated. The station now has a portable high-frequency set which is used for electrical treatment of steam pipe welds in various parts of the station during major overhauls. It is possible to treat 2-3 welds per shift. Measurements were made of the bending of steam pipes during heat treatment of welds. The method of measuring the pipe displacement is explained and test results are given.

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E194/E235

Experience of Introducing the Process of Electrical Heat Treatment of Welded Joints on Steam Piping in the Cherepet' GRES

Analysis of the results shows that induction heat treatment of pipework welds has negligible effects. However, under certain circumstances additional bending stresses may be set up in the pipework during the heating process and it would be best to make the welds whilst the pipework is mounted on spring type suspensions. For successful heat treatment the welds should be at a distance of not less than 1 metre from heavy parts such as flanges, valves and the like. There are 7 figures and 4 tables.

Card 4/4

KOSSOY, M.S., inzh.

Experience in using the thermoelectric treatment for the welded joints of steampipes in the Cherepet Hydroelectric Power Plant. Energomashinostroenie 7 no.3:28-31 Mr '61. (MIRA 16:8)

(Induction hardening)
(Cherepet Hydroelectric Power Station--Steampipes)

KOSSOY, Yu. M., (Gor'kiy)

With the railroad workers of an automobile plant. Put' i put. khoz. no.3:36-37 Mr '57. (MLRA 10:5)

(Gorkiy--Automobile industry)

KOSSOY Yu M

KOSSOY, Yu.M. (g. Gor'kiy).

Automobile chassis for mobile power generators. Put' i put. khoz. no.1:20 Ja '58. (MIRA 11:1)

1. Nachal'nik sluzhby Gor'kovskogo avtozavoda.
(Vehicles) (Electric generators)

KOSSOY, Yu.M., inzh.(Gor'kiy)

Characteristics of track maintenance and repair in industrial transportation. Zhel.dor.transp. 41 no.12:49-52 D '59.
(MIRA 13:4)

(Railroads, Industrial)

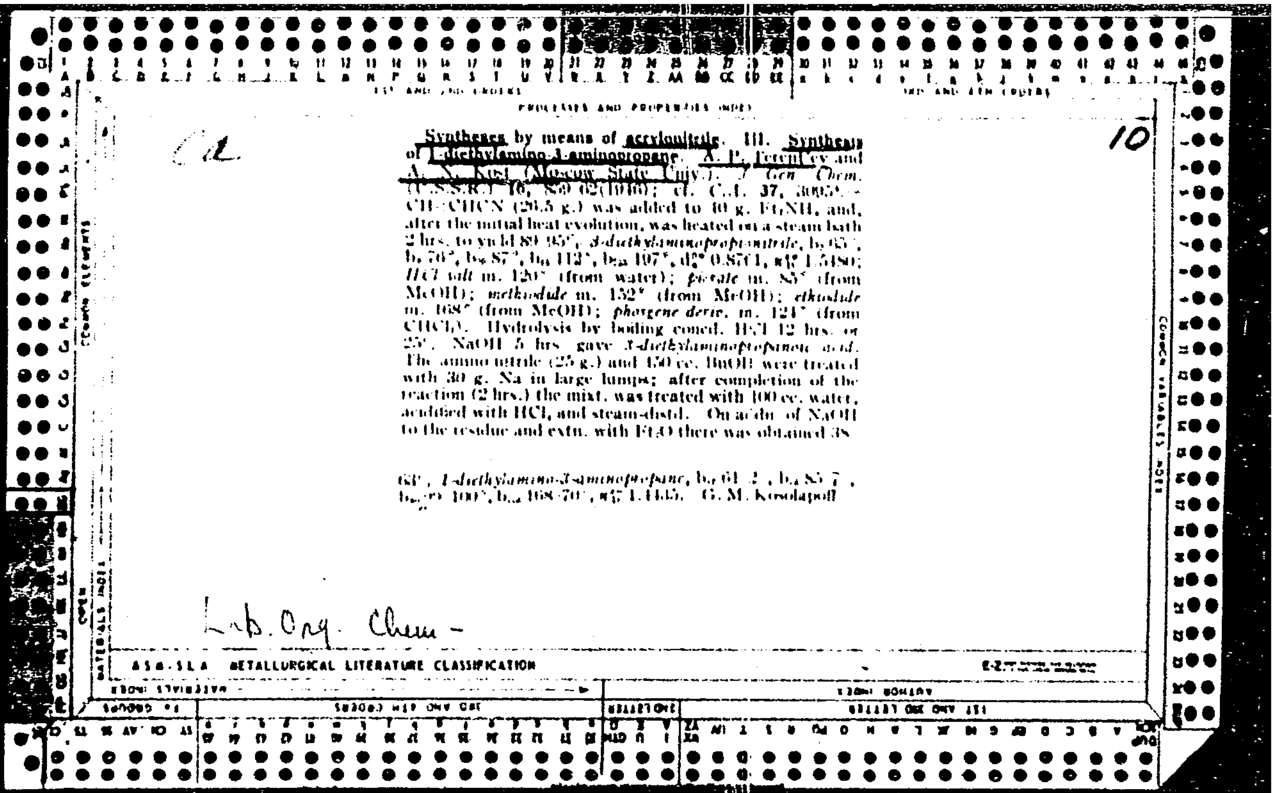
KOSSOY, Yu.M., inzh.

Industrial railroad transportation should be provided with high quality equipment and personnel. Zhel.dor.transp. 42 no.10:63-66 O '60. (MIRA 13:10)

1. Sekretar' partbyuro zheleznodorozhnogo tsekha Gor'kovskogo avtozavoda, g.Gor'kiy.
(Railroads, Industrial)

KOSSOY, Yu.M., inzh. (Gor'kiy)

Organization of track operation, maintenance and repair of the industrial transportation. Zhel. dor. transp. 47 no.1:77-78 Ja '65. (MIRA 18:3)



PROCESSES AND PROPERTIES INDEX

Ca

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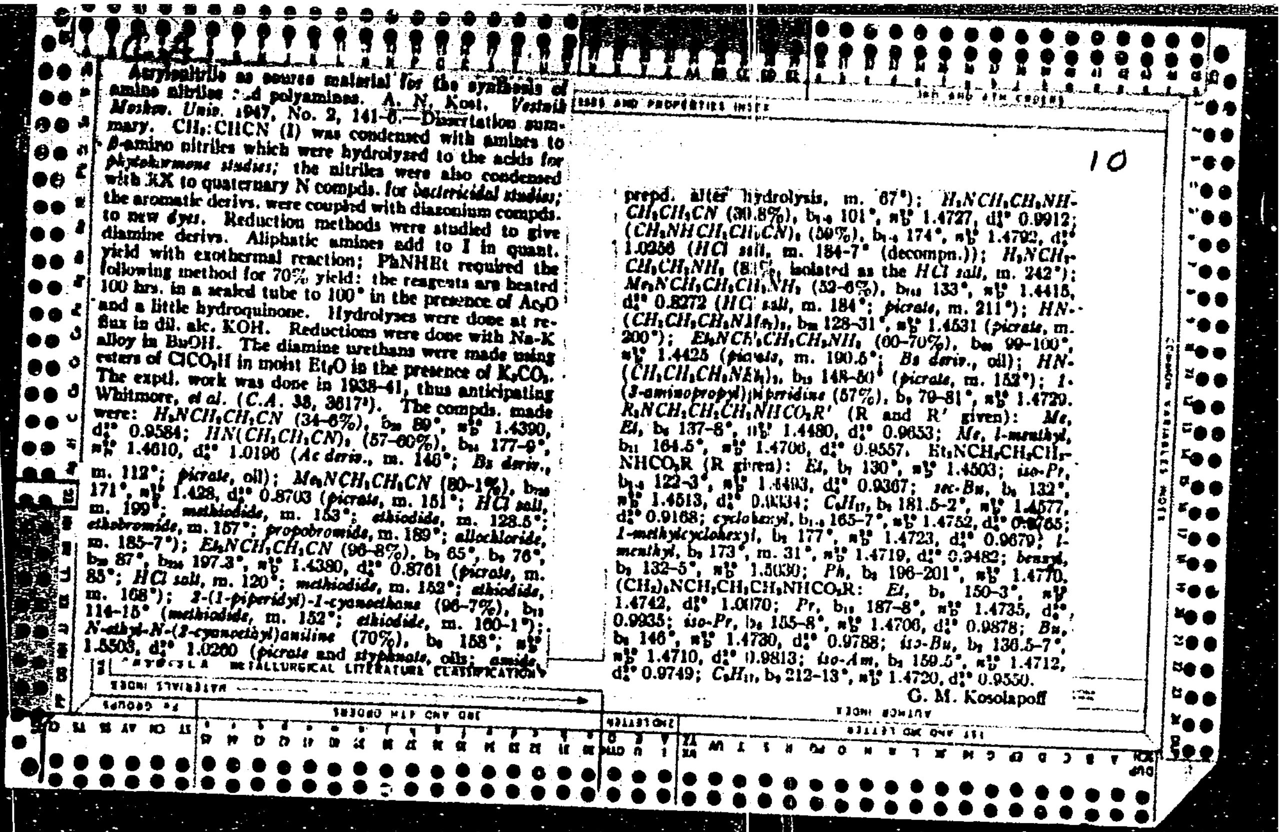
Syntheses by means of acrylonitrile. III. Synthesis of 1-diethylamino-3-aminopropane. A. P. Terent'ev and A. N. Kost (Moscow State Univ.). *J. Gen. Chem.* (U.S.S.R.) 16, 859-62(1946); cf. C.A. 37, 3065⁴.—CH_2:CHCN (26.5 g.) was added to 40 g. Et_2NH, and, after the initial heat evolution, was heated on a steam bath 2 hrs. to yield 80-95%, *3-diethylaminopropionitrile*, b_7 65°, b_{10} 70°, b_{25} 87°, b_{55} 112°, b_{45} 107°, d_4^{20} 0.8761, n_D^{20} 1.5180; *HCl salt* m. 120° (from water); *picrate* m. 85° (from MeOH); *methiodide* m. 132° (from MeOH); *ethiodide* m. 168° (from MeOH); *phosgene deriv.* m. 121° (from $CHCl_3$). Hydrolysis by boiling concd. HCl 12 hrs. or 25% NaOH 5 hrs. gave *3-diethylaminopropionic acid*. The amino nitrile (25 g.) and 150 cc. BuOH were treated with 30 g. Na in large lumps; after completion of the reaction (2 hrs.) the mixt. was treated with 100 cc. water, acidified with HCl, and steam-distd. On addn. of NaOH to the residue and extn. with Et_2O there was obtained 38-68%, *1-diethylamino-3-aminopropane*, b_{14} 61-2°, b_{24} 85-7°, b_{60} 100°, b_{744} 168-70°, n_D^{20} 1.4445. G. M. Kosolapoff

Lab. Org. Chem -

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION


PROCESSES AND PROPERTIES INDEX
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Acrylonitrile as source material for the synthesis of amine nitriles and polyamines. A. N. Kost. *Vestnik Moskov. Univ.* 1947, No. 2, 141-6.—Dissertation summary. $CH_2{:}CHCN$ (I) was condensed with amines to *β*-amino nitriles which were hydrolysed to the acids for *phytohormone studies;* the nitriles were also condensed with RX to quaternary N compds. for *bactericidal studies;* the aromatic derivs. were coupled with diazonium compds. to new *dyes*. Reduction methods were studied to give diamine derivs. Aliphatic amines add to I in quant. yield with exothermal reaction; PhNHEt required the following method for 70% yield: the reagents are heated 100 hrs. in a sealed tube to 100° in the presence of Ac_2O and a little hydroquinone. Hydrolyses were done at reflux in dil. alc. KOH. Reductions were done with Na-K alloy in BuOH. The diamine urethans were made using esters of $ClCO_2H$ in moist Et_2O in the presence of K_2CO_3. The exptl. work was done in 1938-41, thus anticipating Whitmore, *et al.* (*C.A.* 38, 3617^4). The compds. made were: $H_2NCH_2CH_2CN$ (34-6%), b_{20} 89°, n_D^{20} 1.4390, d_4^{20} 0.9584; $HN(CH_2CH_2CN)_2$ (57-60%), b_{14} 177-9°, n_D^{20} 1.4610, d_4^{20} 1.0196 (*Ac deriv.*, m. 146°; *Bz deriv.*, m. 112°; *picrate*, oil); $Me_2NCH_2CH_2CN$ (80-1%), b_{750} 171°, n_D^{20} 1.428, d_4^{20} 0.8703 (*picrate*, m. 151°; *HCl salt*, m. 199°; *methiodide*, m. 153°; *ethiodide*, m. 128.5°; *ethobromide*, m. 157°; *propobromide*, m. 189°; *allochloride*, m. 185-7°); $Et_2NCH_2CH_2CN$ (96-8%), b_3 65°, b_6 76°, b_{20} 87°, b_{750} 197.3°, n_D^{20} 1.4380, d_4^{20} 0.8761 (*picrate*, m. 85°; *HCl salt*, m. 120°; *methiodide*, m. 152°; *ethiodide*, m. 168°); *2-(1-piperidyl)-1-cyanoethane* (96-7%), b_{12} 114-15° (*methiodide*, m. 152°; *ethiodide*, m. 160-1°); *N-ethyl-N-(2-cyanoethyl)aniline* (70%), b_3 158°, n_D^{20} 1.5503, d_4^{20} 1.0260 (*picrate* and *styphnate*, oils; *amide* prepd. after hydrolysis, m. 67°); $H_2NCH_2CH_2NHCH_2CH_2CN$ (30.8%), $b_{1.0}$ 101°, n_D^{20} 1.4727, d_4^{20} 0.9912; $(CH_2NHCH_2CH_2CN)_2$ (59%), $b_{1.0}$ 174°, n_D^{20} 1.4792, d_4^{20} 1.0256 (*HCl salt*, m. 184-7° (decompn.)); $H_2NCH_2CH_2CH_2NH_2$ (81%, isolated as the *HCl salt*, m. 242°); $Me_2NCH_2CH_2CH_2NH_2$ (52-6%), b_{10} 133°, n_D^{20} 1.4415, d_4^{20} 0.8272 (*HCl salt*, m. 184°; *picrate*, m. 211°); $HN(CH_2CH_2CH_2NMe_2)_2$, b_{20} 128-31°, n_D^{20} 1.4531 (*picrate*, m. 200°); $Et_2NCH_2CH_2CH_2NH_2$ (60-70%), b_{20} 99-100°, n_D^{20} 1.4425 (*picrate*, m. 190.5°; *Bz deriv.*, oil); $HN(CH_2CH_2CH_2NEt_2)_2$, b_{10} 148-50° (*picrate*, m. 152°); *1-(3-aminopropyl)piperidine* (57%), b_8 79-81°, n_D^{20} 1.4720. $R_2NCH_2CH_2CH_2NHCO_2R'$ (R and R′ given): *Me, Et*, b_4 137-8°, n_D^{20} 1.4480, d_4^{20} 0.9653; *Me, l-menthyl*, b_{11} 164.5°, n_D^{20} 1.4706, d_4^{20} 0.9557. $Et_2NCH_2CH_2CH_2NHCO_2R$ (R given): *Et*, b_7 130°, n_D^{20} 1.4503; *iso-Pr*, $b_{1.0}$ 122-3°, n_D^{20} 1.4493, d_4^{20} 0.9307; *sec-Bu*, b_4 132°, n_D^{20} 1.4513, d_4^{20} 0.9334; C_5H_{11}, b_4 181.5-2°, n_D^{20} 1.4577, d_4^{20} 0.9168; *cyclohexyl*, $b_{1.0}$ 165-7°, n_D^{20} 1.4752, d_4^{20} 0.9765; *1-methylcyclohexyl*, b_4 177°, n_D^{20} 1.4723, d_4^{20} 0.9679; *l-menthyl*, b_4 173°, m. 31°, n_D^{20} 1.4719, d_4^{20} 0.9482; *benzyl*, b_3 132-5°, n_D^{20} 1.5030; *Ph*, b_4 196-201°, n_D^{20} 1.4770. $(CH_2)_5NCH_2CH_2CH_2NHCO_2R$: *Et*, b_4 150-3°, n_D^{20} 1.4742, d_4^{20} 1.0070; *Pr*, b_{10} 187-8°, n_D^{20} 1.4735, d_4^{20} 0.9935; *iso-Pr*, b_4 155-8°, n_D^{20} 1.4706, d_4^{20} 0.9878; *Bu*, b_4 146°, n_D^{20} 1.4730, d_4^{20} 0.9788; *iso-Bu*, b_4 136.5-7°, n_D^{20} 1.4710, d_4^{20} 0.9813; *iso-Am*, b_4 159.5°, n_D^{20} 1.4712, d_4^{20} 0.9749; C_5H_{11}, b_4 212-13°, n_D^{20} 1.4720, d_4^{20} 0.9550.

G. M. Kosolapoff

PROCESSES AND PROPERTIES INDEX

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Syntheses with acrylonitrile. IV. Reduction of nitriles with sodium in alcohol medium. A. N. Kost and A. P. Terent'ev (Moscow State Univ.). *J. Gen. Chem.* (U.S.S.R.) 17, 105-8(1947)(in Russian); cf. *C.A.* 41, 1000k.—In unpublished work of Longinov and Filippov (1935) it was found that when the Na used for the reduction of esters contains even as little as 0.01% of K the yields of the alcs. drop rapidly. In the reduction of BuCH(CO$_2$Et)$_2$ the yield is zero when the Na contains 0.1% K. However, if the amt. of K is increased, the yields rise again and become normal with 2% K. This is important since Na is usually contaminated with traces of K. This study was extended to the reduction of Et$_2$NCH$_2$CH$_2$CN and 1-piperidinepropionitrile in BuOH by the method of Suter and Moffett (*C.A.* 28, 1659^1). Tech. Na gave 38-60% of the diamine, pure Na 51-63%, while tech. Na with the addn. of 2% K gave 65.9-70% diamine, in the case of Et$_2$NCH$_2$CH$_2$CN. With the piperidyl compd. the yields were 42-46%, 48.9-57.2%, and 48-57%, resp., thus indicating a similarity to the results obtained in ester reduction. The high-K Na gave reproducible yields and tended to give smaller amts. of higher-boiling products (presumably secondary amines). The Rupe technique (immediate steam distn.) gave similar results, but was inconvenient because of the low volatility of the products. G. M. K.

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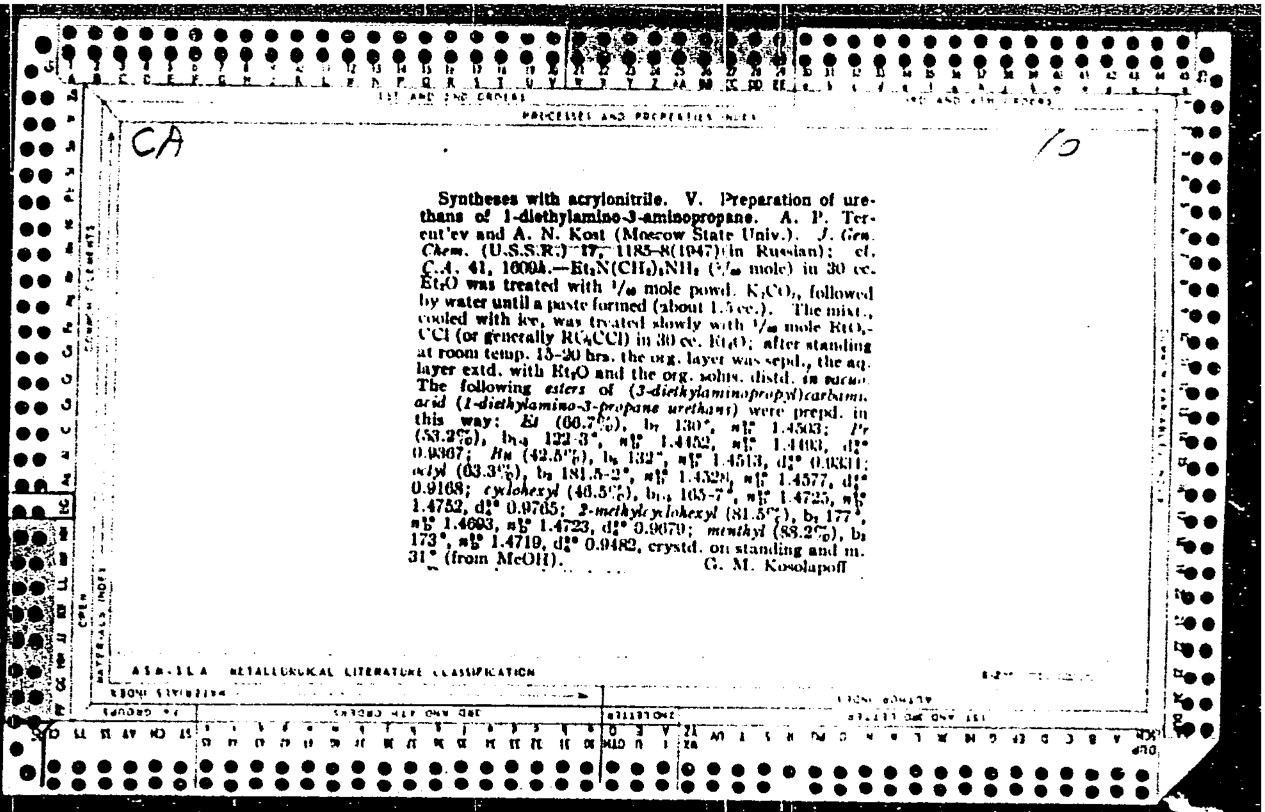

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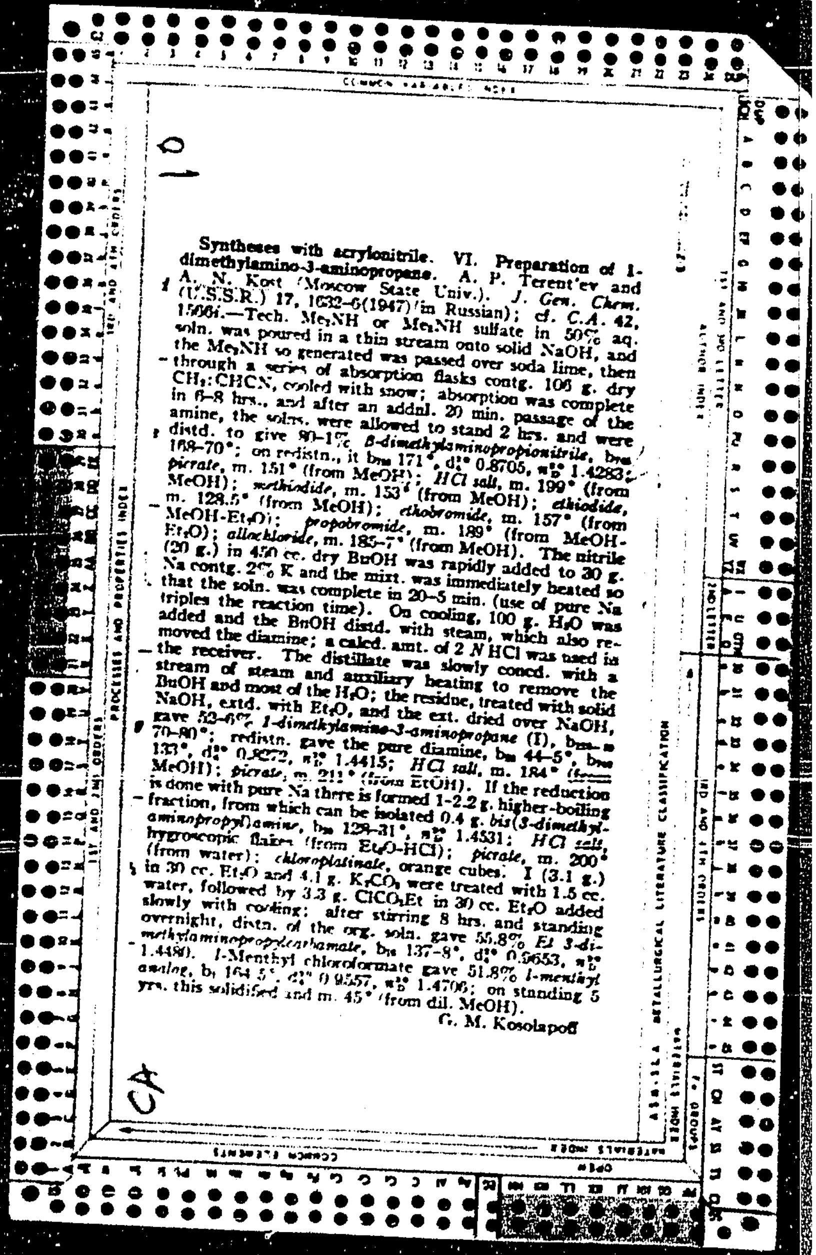
Syntheses with acrylonitrile. V. Preparation of urethans of 1-diethylamino-3-aminopropane. A. P. Terent'ev and A. N. Kost (Moscow State Univ.). *J. Gen. Chem.* (U.S.S.R.) 17, 1185-8(1947)(in Russian); cf. *C.A.* 41, 1600h.—$Et_2N(CH_2)_3NH_2$ ($^1/_{10}$ mole) in 30 cc. Et_2O was treated with $^1/_{10}$ mole powd. K_2CO_3, followed by water until a paste formed (about 1.5 cc.). The mixt., cooled with ice, was treated slowly with $^1/_{10}$ mole RO_2CCl (or generally RO_2CCl) in 30 cc. Et_2O; after standing at room temp. 15-20 hrs. the org. layer was sepd., the aq. layer extd. with Et_2O and the org. solns. distd. *in vacuo*. The following *esters* of *(3-diethylaminopropyl)carbamic acid (1-diethylamino-3-propane urethans)* were prepd. in this way: *Et* (60.7%), b_7 130°, n_D^{20} 1.4503; *Pr* (53.2%), $b_{0.5}$ 122-3°, n_D^{15} 1.4452, n_D^{20} 1.4403, d_4^{20} 0.9907; *Bu* (42.5%), b_6 132°, n_D^{20} 1.4513, d_4^{20} 0.9811; *octyl* (63.3%), b_6 181.5-2°, n_D^{15} 1.4529, n_D^{20} 1.4577, d_4^{20} 0.9168; *cyclohexyl* (46.5%), $b_{0.5}$ 165-7°, n_D^{15} 1.4725, n_D^{20} 1.4752, d_4^{20} 0.9705; *2-methylcyclohexyl* (81.5%), b_7 177°, n_D^{15} 1.4693, n_D^{20} 1.4723, d_4^{20} 0.9670; *menthyl* (83.2%), b_3 173°, n_D^{20} 1.4719, d_4^{20} 0.9482, crystd. on standing and m. 31° (from MeOH).

G. M. Kosolapoff


ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION
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Syntheses with acrylonitrile. VI. Preparation of 1-
dimethylamino-3-aminopropane. A. P. Terent'ev and
A. N. Kost (Moscow State Univ.). *J. Gen. Chem.*
(U.S.S.R.) 17, 1632-6(1947)(in Russian); cf. *C.A.* 42,
1506i.—Tech. Me_2NH or Me_2NH sulfate in 50% aq.
soln. was poured in a thin stream onto solid NaOH, and
the Me_2NH so generated was passed over soda lime, then
through a series of absorption flasks contg. 106 g. dry
$CH_2:CHCN$, cooled with snow; absorption was complete
in 6-8 hrs., and after an addnl. 20 min. passage of the
amine, the solns. were allowed to stand 2 hrs. and were
distd. to give 90-1% *β-dimethylaminopropionitrile*, b_{760}
168-70°; on redistn., it b_{760} 171°, d_4^{20} 0.8705, n_D^{20} 1.4283;
picrate, m. 151° (from MeOH); *HCl salt*, m. 199° (from
MeOH); *methiodide*, m. 153° (from MeOH); *ethiodide*,
m. 128.5° (from MeOH); *ethobromide*, m. 157° (from
MeOH-Et_2O); *propobromide*, m. 189° (from MeOH-
Et_2O); *allochloride*, m. 185-7° (from MeOH). The nitrile
(20 g.) in 450 cc. dry BuOH was rapidly added to 30 g.
Na contg. 2% K and the mixt. was immediately heated so
that the soln. was complete in 20-5 min. (use of pure Na
triples the reaction time). On cooling, 100 g. H_2O was
added and the BuOH distd. with steam, which also re-
moved the diamine; a calcd. amt. of 2 *N* HCl was used in
the receiver. The distillate was slowly concd. with a
stream of steam and auxiliary heating to remove the
BuOH and most of the H_2O; the residue, treated with solid
NaOH, extd. with Et_2O, and the ext. dried over NaOH,
gave 53-6% *1-dimethylamino-3-aminopropane* (I), b_{760}
70-80°; redistn. gave the pure diamine, b_{20} 44-5°, b_{760}
133°, d_4^{20} 0.8272, n_D^{20} 1.4415; *HCl salt*, m. 184° (from
MeOH); *picrate*, m. 211° (from EtOH). If the reduction
is done with pure Na there is formed 1-2.2 g. higher-boiling
fraction, from which can be isolated 0.4 g. *bis(3-dimethyl-*
aminopropyl)amine, b_{20} 128-31°, n_D^{20} 1.4531; *HCl salt*,
hygroscopic flakes (from Et_2O-HCl); *picrate*, m. 200°
(from water); *chloroplatinate*, orange cubes. I (3.1 g.)
in 30 cc. Et_2O and 4.1 g. K_2CO_3 were treated with 1.5 cc.
water, followed by 3.3 g. $ClCO_2Et$ in 30 cc. Et_2O added
slowly with cooling; after stirring 8 hrs. and standing
overnight, distn. of the org. soln. gave 55.8% *Et 3-di-*
methylaminopropylcarbamate, b_{16} 137-8°, d_4^{20} 0.9653, n_D^{20}
1.4480). *l*-Menthyl chloroformate gave 51.8% *l-menthyl*
analog, b_7 164.5°, d_4^{20} 0.9557, n_D^{20} 1.4706; on standing 5
yrs. this solidified and m. 45° (from dil. MeOH).

G. M. Kosolapoff

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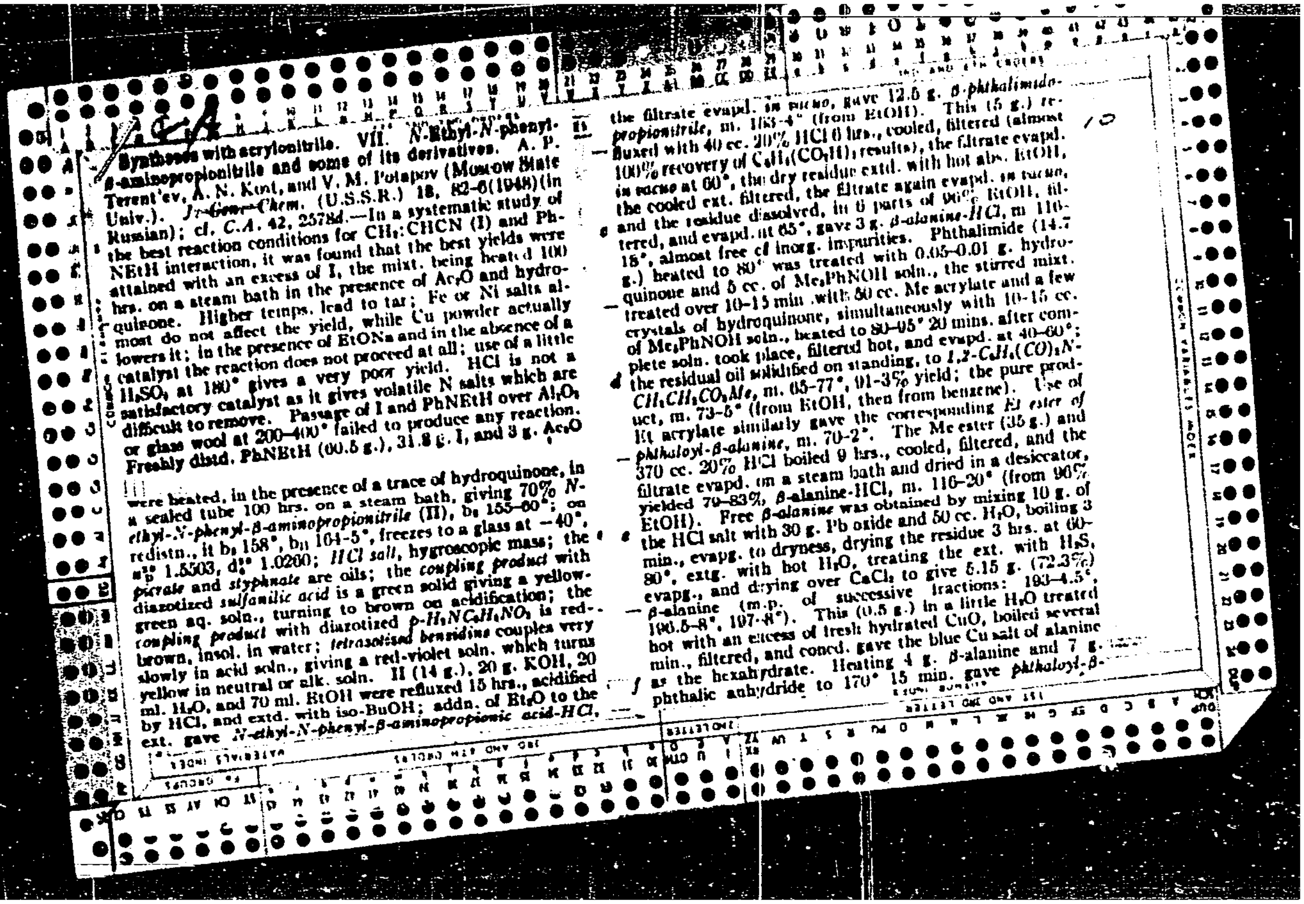

Syntheses with acrylonitrile. VII. *N*-Ethyl-*N*-phenyl-β-aminopropionitrile and some of its derivatives. A. P. Terent'ev, A. N. Kost, and V. M. Potapov (Moscow State Univ.). *J. Gen. Chem.* (U.S.S.R.) 18, 82-6(1948)(in Russian); cf. *C.A.* 42, 2578d.—In a systematic study of the best reaction conditions for $CH_2:CHCN$ (I) and PhNEtH interaction, it was found that the best yields were attained with an excess of I, the mixt. being heated 100 hrs. on a steam bath in the presence of Ac_2O and hydroquinone. Higher temps. lead to tar; Fe or Ni salts almost do not affect the yield, while Cu powder actually lowers it; in the presence of EtONa and in the absence of a catalyst the reaction does not proceed at all; use of a little H_2SO_4 at 180° gives a very poor yield. HCl is not a satisfactory catalyst as it gives volatile N salts which are difficult to remove. Passage of I and PhNEtH over Al_2O_3 or glass wool at 200-400° failed to produce any reaction. Freshly distd. PhNEtH (60.5 g.), 31.8 g. I, and 3 g. Ac_2O were heated, in the presence of a trace of hydroquinone, in a sealed tube 100 hrs. on a steam bath, giving 70% *N-ethyl-N-phenyl-β-aminopropionitrile* (II), b_8 155-60°; on redistn., it b_8 158°, b_{11} 164-5°, freezes to a glass at −40°, n^{20}_D 1.5503, d^{20}_4 1.0200; *HCl salt*, hygroscopic mass; the *picrate* and *styphnate* are oils; the *coupling product* with diazotized *sulfanilic acid* is a green solid giving a yellow-green aq. soln., turning to brown on acidification; the *coupling product* with diazotized *p-$H_2NC_6H_4NO_2$* is red-brown, insol. in water; *tetrazotized benzidine* couples very slowly in acid soln., giving a red-violet soln. which turns yellow in neutral or alk. soln. II (14 g.), 20 g. KOH, 20 ml. H_2O, and 70 ml. EtOH were refluxed 15 hrs., acidified by HCl, and extd. with iso-BuOH; addn. of Et_2O to the ext. gave *N-ethyl-N-phenyl-β-aminopropionic acid-HCl*, the filtrate evapd. *in vacuo*, gave 12.5 g. *β-phthalimidopropionitrile*, m. 153-4° (from EtOH). This (5 g.) refluxed with 40 cc. 20% HCl 6 hrs., cooled, filtered (almost 100% recovery of $C_6H_4(CO_2H)_2$ results), the filtrate evapd. *in vacuo* at 60°, the dry residue extd. with hot abs. EtOH, the cooled ext. filtered, the filtrate again evapd. *in vacuo*, and the residue dissolved, in 6 parts of 96% EtOH, filtered, and evapd. at 65°, gave 3 g. *β-alanine-HCl*, m. 110-15°, almost free of inorg. impurities. Phthalimide (14.7 g.) heated to 80° was treated with 0.05-0.01 g. hydroquinone and 5 cc. of Me_3PhNOH soln., the stirred mixt. treated over 10-15 min. with 50 cc. Me acrylate and a few crystals of hydroquinone, simultaneously with 10-15 cc. of Me_3PhNOH soln., heated to 80-95° 20 mins. after complete soln. took place, filtered hot, and evapd. at 40-60°; the residual oil solidified on standing, to *1,2-$C_6H_4(CO)_2N$-$CH_2CH_2CO_2Me$*, m. 65-77°, 91-3% yield; the pure product, m. 73-5° (from EtOH, then from benzene). Use of Et acrylate similarly gave the corresponding *Et ester of phthaloyl-β-alanine*, m. 70-2°. The Me ester (35 g.) and 370 cc. 20% HCl boiled 9 hrs., cooled, filtered, and the filtrate evapd. on a steam bath and dried in a desiccator, yielded 79-83% β-alanine-HCl, m. 116-20° (from 96% EtOH). Free *β-alanine* was obtained by mixing 10 g. of the HCl salt with 30 g. Pb oxide and 50 cc. H_2O, boiling 3 min., evapg. to dryness, drying the residue 3 hrs. at 60-80°, extg. with hot H_2O, treating the ext. with H_2S, evapg., and drying over $CaCl_2$ to give 5.15 g. (72.3%) β-alanine (m.p. of successive fractions: 193-4.5°, 196.5-8°, 197-8°). This (0.5 g.) in a little H_2O treated hot with an excess of fresh hydrated CuO, boiled several min., filtered, and concd. gave the blue Cu salt of alanine as the hexahydrate. Heating 4 g. β-alanine and 7 g. phthalic anhydride to 170° 15 min. gave *phthaloyl-β-*

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[illegible] II, m. 194-5° (decompn.); this results also from III and EtCOCl with 3-methylpyridine in 34% yield. III and BzH give 64% of the benzylidene analog, m. 166°. II (1 g.), refluxed 1 hr. with 50 ml. H_2O, gives 93% $AcCH_2NHBz$, m. 84° (*2,4-dinitrophenylhydrazone*, golden, m. 214-15°). I (1 g.), refluxed 2 hrs. with 100 ml. abs. EtOH, gives a quant. yield of $AcCH(CO_2Et)NHBz$, b. 150°/10^{-4} mm. (5-10% reconversion to I) (*semicarbazone*, m. 172-3° (decompn., not cor.)). $MeCH(NHBz)CO_2Na$ (5 g.) and 7.5 ml. Ac_2O, heated 5 min. at 100°, give 1.5 g. 2-phenyl-4-methyl-5(4*H*)-oxazolone and 1 g. *Me 1-benzamidoethyl ketone*, pale yellow, b.[illegible] 116-30° (*2,4-dinitrophenylhydrazone*, pale yellow, m. 199-200° (not cor.)); in a 2nd expt. (heating 1 min. at 100°), there resulted a compd. $C_{20}H_{19}O_4N_3$, m. 225-6° (decompn., not cor.). II could not be reduced in aq. soln. with Pt oxide or small quantities of Raney Ni. II (2 g.) in 20 ml. 0.5 *N* NaOH and 4 g. Raney Ni, shaken 20 hrs. with H at room temp. and atm. pressure (4 mols. H absorbed), give 54.5% $MeCH(OH)CH(NH_2)CO_2H$ (V), m. 238-9°; microbiol. assay showed that this contained about 7% DL-threonine (VI). II (10 g.) in 110 ml. 0.5 *N* NaOH, hydrogenated over 20 g. Raney Ni until 1 atom H was absorbed, gave 6 g. unchanged II and 2.6 g. (63% on basis of II consumed) DL-*N-benzylallothreonine*, m. 238° (decompn.); further reduction in *N* NaOH over Raney Ni (12 hrs.) gave 70% V. II (20 g.) in 200 ml. 0.5 *N* NaOH, hydrogenated (2 hrs.) over 20 g. Raney Ni at 85-90°/110 atm. and the crude product (7.5 g.) extd. with 15 ml. H_2O, give, on addn. of 100 ml. hot alc. to the filtrate, 3 g. V; the insol. portion (4.2 g.), crystd. repeatedly from AcOH, yields *α-[(cyclohexylmethyl)amino]-β-hydroxybutyric acid* (VII), m. 231-2°; reduction at 100-10°/125 atm. gives only VII. VII (1 g.), 7 ml. HI, and 0.17 g. red P, heated 6 hrs. at 160°, give 65% *α-[(cyclohexylmethyl)amino]butyric acid*, m. 300-2° (decompn. and sublimation); *HCl salt*, m. 211-13° (decompn.); *Et ester-HCl*, m. 128-30°; the acid was prepd. also in 67% yield from (cyclohexylmethyl)amine and $EtCHBrCO_2H$. $AcCH(CO_2Et)NHBz$ (220 g.) and 880 ml. abs. EtOH, refluxed 1 hr., 15 g. Raney Ni added, the refluxing continued 30 min., the filtrate hydrogenated (1-3 hrs.) over 50 g. Raney Ni at 100°/75-100 atm., and the crude HO ester (97%) hydrolyzed with HBr, gives 64% V (on basis of hippuric acid); the ester b. 110°/10^{-4} mm. and partially crystd., the crystals being used to seed the crude ester. The ester (265 g.) in 1.1 l. ether, allowed to stand 3 days at 0°, gives 104 g. (38% based on II) DL-*N-benzoylallothreonine Et ester* (VIII), m. 98.5-101.5°; mild alk. hydrolysis gives 93% DL-*N-benzoylallothreonine* (IX), m. 177°. The ethereal filtrate yields 108 g. of a yellow oil, which yields 66 g. (18% on basis of II) of the $PhCH_2CH_2NH_2$ salt (m. 161-2°), decompn. of which gives 13% DL-*N*-benzoylthreonine (on basis of II) and (with HBr) about 12% of DL-threonine. VIII (240 g.) in 850 ml. dry C_5H_5N at −10°, treated with 192 g. *p*-$MeC_6H_4SO_2Cl$ (3.5 hrs.) and poured into 1.2 l. concd. HCl and 2.4 kg. ice, gives 270 g. DL-*N-benzoyl-O-(p-tosyl)allothreonine Et ester* (X), m. 82.5-3° (from petr. ether) or 148.5-51.5° (from AcOEt-petr. ether); 270 g. crude X, 138 g. AcOK, and 950 ml. anhyd. EtOH, refluxed 2.5 hrs., give 30% (on basis of II) of DL-*trans-4-carbethoxy-2-phenyl-5-methyl-Δ²-oxazoline* (XI), $MeCH.CH(CO_2Et).N:CPh.O$, b. 100°/10^{-4} mm.; *picrate*, m. 127.3°; *HCl salt*, m. 117.5-18°; 150 g. XI and 750 ml. 23% HBr, refluxed 4 hrs. and the sirupy residue dissolved in 750 ml. hot EtOH and a slight excess of concd. NH_4OH, give 56 g. (26% on basis of II) of VI. VIII (20 g.) and 50 ml. $SOCl_2$, kept 1 hr. at room temp., give 33% (based on II) of a mixt. of *cis*- and *trans*-XI; the HCl salt, on standing in the air, absorbs H_2O and gives DL-*O-benzoylthreonine Et ester-HCl*, m. 167°; *picrate*, bright yellow, m. 140.5°. DL-Allothreonine has no effect on the growth of *Strep. faecalis* in the presence or absence of VI. NH_4Br, a possible contaminant of crude samples of the amino acid, also is without effect on the growth of the organism. The total over-all yield of VI from hippuric acid is about 30%, the greatest loss being incurred during the sepn. of the HO ester.

C. J. West

KOST, A. N.

USSR/Chemistry - Propionitrile, Beta
(N-Piperidyl)
Chemistry - Synthesis

Mar 1948

"Synthesis With the Aid of Nitrile Acrylic Acid. VIII. 1-(1'-Piperidyl)-3-Amino-Propane and Its Urethan Derivatives," A. P. Terent'yev, A. N. Kost, Lab Org Chem imeni Academician N. D. Zelinskiy, Moscow State U, 5 pp

"Zhur Obshch Khim" Vol XVIII (LXXX), No 3

Piperidine and acrylonitrile were used to product beta-(N-piperidyl)-propionitrile. Latter was reduced by sodium potassium alloys to produce 1-(1'-piperidyl)-3-amino-propane. Article describes properties of some eight new compounds. Submitted 24 Feb 1947.

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Synthesis of 1-oxa-5-azacyclooctane. A. N. Kost, A. P. Terent'ev, and V. G. Yashunskii. *Vestnik Moskov. Univ.* 5, No. 6, *Ser. Fiz.-Mat. i Estest. Nauk* No. 4, 41-2(1950).—Condensation of $CH_2:CHCN$ and $HOCH_2CH_2CN$ with aq. KOH catalyst gave 88.7% $O(CH_2CH_2CN)_2$. This, reduced with Na and BuOH, upon prolonged steam distn., acidification of the distillate, evapn., and treatment with solid NaOH, gave 32.8% cyclic base, $C_6H_{13}NO$, b_{760} 167-8°, b_{16} 60-2°, d_4^{20} 0.9832, n_D^{20} 1.4288, which contained approx. the correct amt. of active H required by $O(CH_2CH_2CH_2)_2NH$. The product has high affinity for CO_2 and fumes in air. Its *HCl salt* is very hygroscopic; *picrate*, m. 96°; *1-naphthylureide*, m. 117-18°; *chloroplatinate*, decomp. 119° (from H_2O); the *styphnate* and *benzenesulfonamide derivs.* are oils. The amt. of NH_3 liberated during the reduction approximates the yield of the cyclic amine (12.5% of total N of the diamine).

G. M. Kosolapoff

1951

CA KOST, A.N.

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Action of organomagnesium compounds on acrylonitrile. A. P. Terent'ev and A. N. Kost. *Vestnik Moskov. Univ.* 5, No. 8, *Ser. Fiz.-Mat. i Estestven. Nauk* No. 5, 41-3(1950). Addn. of MeMgI, EtMgBr, BuMgCl, PhMgBr, or PhCH$_2$MgCl in Et$_2$O at room temp. to CH$_2$:CHCN causes spontaneous polymerization of anionoid type of the latter; a 100% yield of ppt. forms even at −10° almost instantaneously. The polymer, after washing and pptn. from pyridine by H$_2$O, is a light yellow solid, sol. in pyridine, iso-AmOAc, and MeNO$_2$, softening at 160-80°, Rast mol. wt. about 900. Metallic Na does not react with CH$_2$:CHCN even after 100 hrs. at 90°. G. M. Kosolapoff

KOST, A.N., SHVEKHGEYMER, G.A.

Amines

Preparation of some N-derivatives of cyclopentylamine. Vest. Mosk. un., 5, No. 9, 1950.

9. Monthly List of Russian Accessions, Library of Congress, October, 1952 ~~1952x~~ Unclassified.

KOST, A. N.

A. P. Terent'ev, K. I. Chursina, and A. N. Kost - "Syntheses with acrylonitrile. IX. The reaction of acrylonitrile with ammonia and the formation of trimethylene diamine." (p. 1073)

SO: Journal of General Chemistry, (Zhurnal Obshchei Khimii), 1950, Vol. 20, No. 6.

CA

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Syntheses with acrylonitrile. XI. Cyanoethylation of ethylenediamine. A. P. Terent'ev and A. N. Kost (Moscow State Univ.). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 20, 2069-71(1950); cf. C.A. 42, 7267*f*. 44, 9349*f*. Addn. of 35 g. dry CH_2:CHCN with stirring and good cooling to 20 g. dry $(CH_2NH_2)_2$ in 50 ml. Et_2O at 15-20° (2 hrs.), stirring 2 hrs., and letting stand overnight in a closed vessel gave 15 g. (39.8%) $H_2N(CH_2)_2NH(CH_2)_2CN$, b_{4-5} 101°, d_4^{20} 0.9912, n_D^{20} 1.4727, and 33.1 g. (59.8%) $(CH_2NHCH_2CH_2CN)_2$, b_{1-2} 174°, b_{4-5} 191°, d_4^{20} 1.0256, n_D^{20} 1.4793. The former yields an oily *picrate* and *mono-Bz deriv.*, while its *HCl salt* is a very hygroscopic solid. the dicyanoethylation product forms an oily *picrate* and a *HCl salt*, decomp. 184-7° (from dil. MeOH). G. M. Kosolapoff

KOST, A.N.

abs

10Oct'55

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Acrylonitrile as a starting material for synthesis of amino nitriles and polyamines. A. N. Kost. *Uchenye Zapiski Moskov. Gosudarst. Univ. im. M. V. Lomonosova,* No. 131, 39-97(1950); cf. *C.A.* 41, 1609*h*; 42, 3722*g*.—Dissertation at the University (1946) with complete exptl. a details and bibliography of 109 references. A lab. prepn. of $CH_2{:}CHCN$ (I) was developed as follows. To a hot satd. soln. of 100 g. $SnCl_2$ was added 30 g. Zn dust with stirring and, after completion of reaction, the mixt. was allowed to stand 2 hrs., decanted, washed with 10% AcOH, let stand overnight with 60 ml. 80-90% AcOH, filtered, washed with H_2O until neutral, and washed with EtOH and Et_2O, giving 30-35 g. Sn dust. All traces of Zn must be removed for good results with this catalyst. Heating 50 g. b $HOCH_2CH_2CN$ with 5 g. of the above Sn dust in a distn. app. with chilled receiver so that vapor temp. is below 110° yields a 2-layer distillate; the upper layer after drying with $CaCl_2$ yields up to 90% I. If com. ethylene oxide is used in the prepn. of the cyanohydrin, the product may be contaminated with $MeCH{:}CHCN$, H_2O, and NH_3; it is purified by 5-10 min. treatment with P_2O_5 and distn. (b_{25} 78°). Refluxing the cyanohydrin with silica gel, activated C, $MgSO_4$, Fe oxides, pieces of sheet Fe, Al foil, and Al_2O_3 gave but 0-30% yields of I. Passage of the cyanohydrin c over Al_2O_3 at 200-20° gave but 18-20% I. To 950 ml. aq. NH_4OH (satd. in the cold) was added 95 g. I dropwise with cooling over 2 hrs. so that the mixt. remained homogeneous; after 30 min. at room temp., distn. gave 50% *$H_2NCH_2CH_2CN$*, b_{14} 77-8°, b_{25} 89°, n_D^{20} 1.4390, d_{20} 0.9584, which polymerized in several days in a sealed ampul even in darkness. Distn. of the higher-boiling residue gave 47% *$HN(CH_2CH_2CN)_2$*, b_{14} 177-9°, b_{25} 200-11°, n_D^{20} 1.4630, d_{20} 1.0198; *HCl salt*, m. 147-8° (from MeOH); *N-Bz deriv.*, m. 112° d (from MeOH). The free amine generated by addn. of 50% aq. Me_2NH to solid NaOH was fed into 106 g. I with ice cooling over 6-8 hrs., and the mixt. distd. after 2 hrs. at room temp. yielding 80-1% *$Me_2NCH_2CH_2CN$*, b_{760} 171°, n_D^{20} 1.4283, d_{20} 0.8705; *picrate*, m. 151°; *HCl salt*, m. 190° (from MeOH). A mixt. of 40 g. Et_2NH and 26.5 g. I gave a slight heat evolution after 5-10 min.; refluxed on a steam bath 3 hrs. (yellow color) and distd., it yielded 89-95% *$Et_2NCH_2CH_2CN$*, b_{25} 80-1°. If the heating is done in

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sealed tubes 6–8 hrs. no yellow color is formed and th
yield is nearly 100%; the pure product b$_7$ 65°, b$_{14}$ 76°, b
87°, b$_{44}$ 112°, b$_{755}$ 197.3° (corr.), d$_{20}$ 0.8761, n_D^{20} 1.438
HCl salt, m. 120°; *picrate*, m. 85°. This (3.1 g.) reflux
4 hrs. with [illegible] NaOH and evapd. gave the amorpho
Na salt of the corresponding acid; refluxing 6.3 g. of th
nitrile with 11 g. concd. HCl, cooling, filtering, and evap
repeatedly *in vacuo* gave an amorphous mass, which wa
freed in aq. soln. of Cl ion by Ag$_2$CO$_3$, the Ag ion remove
with H$_2$S, and the filtrate evapd., yielding 60% *Et$_2$NCH$_2$*
CH$_2$CO$_2$H, m. 70–5°. The best reaction conditions fo
piperidine and I are as follows: Piperidine (17 g.) and 11.
g. I mixed with cooling in an ampul (cooled until the hea
evolution stopped in 15–20 min.) and heated 4 hrs. on
steam bath, then let stand overnight, gave 90–7% *(CH$_2$)$_5$*
NCH$_2$CH$_2$CN, b$_{12}$ 114–15°; some 22% is formed by re
fluxing 5 g. piperidine with 5 g. HOCH$_2$CH$_2$CN 3 hrs. at
120–50°; if Sn dust is added the yield is 52.5%. An ex
tensive study showed that the reaction of I with PhNHEt is
best carried out by heating in an ampul 100 hrs. on steam
bath in the presence of 3% Ac$_2$O and a little hydroquinone,
when 65–70% *PhEtNCH$_2$CH$_2$CN*, b$_8$ 158°, b$_{11}$ 164–5°, n_D^{20}
1.5503, d$_{20}$ 1.0200, is obtained; *HCl salt*, hygroscopic solid;
picrate, oil; the free base *couples* with *diazotized sulfanilic*
acid even in acid medium and the *coupling product*, isolated
as the Na salt, is a green solid, giving a brown color in acid
soln. Coupling with diazotized *p*-O$_2$NC$_6$H$_4$NH$_2$ gave a
brown product, *C$_{17}$H$_{17}$O$_2$N$_5$*, while *diazotized* [illegible]
reacts only slowly in acidified soln., yielding a red-violet
soln. which turns yellow in neutral or basic soln.; the free
azo deriv. is sol. in org. solvents. Hydrolysis of PhEtN-
CH$_2$CH$_2$CN is very slow with H$_2$O at 100° in a sealed tube;
concd. HCl at room temp. acts slowly and incompletely even
in 48 hrs., while heating at 110–20° leads to loss of PhNH-
Et; heating with 30–40% H$_2$SO$_4$ gives an impure product.
Alk. hydrolysis gives low yields of the corresponding acid.
Refluxing 14 g. PhEtNCH$_2$CH$_2$CN and 20 g. KOH in 20
ml. H$_2$O and 70 ml. EtOH 15 hrs., acidifying with HCl, and
repeatedly extg. with iso-BuOH, adding Et$_2$O to the ext.
gave 83.1% *PhEtNCH$_2$CH$_2$CO$_2$H.HCl*, a high-melting
solid, giving a brown color with FeCl$_3$. This couples even
in acid soln. with *diazotized sulfanilic acid*, yielding a red

[OVER]

azo deriv.; *p-$O_2NC_6H_4N_2Cl$* also couples in acid medium,
giving a red azo deriv. $PhEtNCH_2CH_2CN$ (4.5 g.) added
slowly to 15 ml. concd. H_2SO_4, and the mixt. let stand 40
hrs., then dild. with H_2O (60 ml.), neutralized with concd.
NH_4OH, and let stand overnight giving a ppt. of *PhEt-* a
$NCH_2CH_2CONH_2$, 68.5-76.5%, m. 55-8° (crude), m. 67°
(from MeOH). I (35 g.) added to 20 g. dry $(CH_2NH_2)_2$
dropwise with cooling at 15-20° over 2 hrs. the mixt. shaken
2 hrs. at room temp. and let stand overnight in a stoppered
flask gave 39.8% *$H_2NCH_2CH_2NHCH_2CH_2CN$*, $b_{1.5}$ 101°,
n_D^{20} 1.4727, d_{20} 0.9012 (with MeZnI at room temp. only the
primary amino group reacts, while at 100° all active H can
be detd.) (the picrate and styphnate are oils, while HCl salt
is a viscous mass), and 59.8% *$(CH_2NHCH_2CH_2CN)_2$*, $b_{1.5}$ b
174°, $b_{1.5}$ 191°, n_D^{20} 1.4793, d_{20} 1.0250 [*picrate* and *styphnate*,
oils; *HCl salt*, m. 184-7° (decompn.)]. The structure of
the latter appears confirmed by the improbability of reaction
of I with a cyanoethylated group, and further by the reac-
tion with MeZnI which indicates 1.94 active H atoms/mole
at 100° and 0.5 at room temp. *$Me_2NCH_2CH_2CN$* treated
with MeI in C_6H_6 with cooling gave the *methiodide*, m. 183°
(from MeOH); EtI at room temp. yielded the *ethiodide*,
m. 128.5° (from MeOH); EtBr at 60° yielded the *etho-* c
bromide, m. 157° (from Et_2O-MeOH); PrBr and $CH_2:CH$-
CH_2Cl at 80° yielded the corresponding *quaternary salts*, m.
189° (from Et_2O-MeOH), and 185-7° (from MeOH), resp.
$Et_2NCH_2CH_2CN$ with MeI at room temp. gave the *meth-*
iodide, m. 152° (from MeOH), while EtI at 60° gave the
ethiodide, m. 108° (from MeOH). *$(CH_2)_5NCH_2CH_2CN$*
with MeI at 100° gave the *methiodide*, m. 163° (from
MeOH), while EtI reacted slowly at 100° yielding the
ethiodide, m. 180-1° (from MeOH). Reduction of H_2N-
CH_2CH_2CN with BuOH-Na gave variable yields when com. d
Na was used, because of traces of K (Dzirkal, *C.A.* 36,
2255^4); a 2% K-Na alloy gave high yields comparable to
those obtained with pure Na. In the best procedure 30 g.
of this alloy was rapidly treated with 14 g. $H_2NCH_2CH_2CN$
in 450 ml. BuOH, and despite vigorous reaction the mixt.
was immediately heated in an oil bath at 140-50°, cooled
after 35-40 min., dild. with 130-50 ml. cold H_2O, steam-
distd. 4-6 hrs. into the calcd. amt. of aq. HCl, and the
distillate evapd., yielding 81% *$CH_2(CH_2NH_2)_2.2HCl$*, m. e

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312° (from EtOH). Similar reduction of $Me_2NCH_2CH_2CN$ gave 52-6% $Me_2NCH_2CH_2CH_2NH_2$, b_{18-20} 70-80° (crude), b_{20} 44-5°, b_{760} 133°, n_D^{20} 1.4415, d_{20} 0.8272; *di-HCl salt*, m. 184° (from MeOH); *picrate*, $C_{17}H_{20}N_8O_{14}$, m. 211° (from H_2O). The higher-boiling material yielded a little *3,3'-bis(dimethylamino)dipropylamine*, b_{20} 128-31°, n_D^{20} 1.4531 (*HCl salt*, hygroscopic solid; *tripicrate*, m. 200°; *chloroplatinate*, $2C_{10}H_{25}N_3.3H_2PtCl_6$, sol. in H_2O, insol. in aq. EtOH). Reduction of $Et_2NCH_2CH_2CN$ with Na-BuOH gave 38-63% diamine; a 2% K-Na alloy gave good consistent 60-70% yields; pure $Et_2NCH_2CH_2CH_2NH_2$, b_{15} 61-2°, b_{70} 85-7°, b_{60} 99-100°, b_{745} 168-70°, n_D^{20} 1.4435, gave 2 active H with MeZnI at room temp. and at 100°; *picrate*, m. 190.5° (from MeOH); *Bz deriv.*, oil. Refluxing this amine with an equimolar amt. of oleic acid 2 hrs., adding a little amine, heating another hr., concg., and evapg. with C_6H_6 gave a product that formed extremely stable org.-aq. emulsions. The higher-boiling fractions from the above reduction gave a little *bis(diethylamino)dipropylamine*, b_2 148-50° (*picrate*, m. 152°), also obtained if the reduction is run with pure Na. Reduction of $(CH_2)_5NCH_2CH_2CN$ with 2% K-Na in BuOH gave 57% *1-(3-aminopropyl)piperidine*, b_4 65-6°, b_9 79-81°, n_D^{20} 1.4729. $COCl_2$ with ROH gave the $ClCO_2R$: R = *Et*, b_{755} 92-4°; *Pr*, b_{752} 114-15°, n_D^{20} 1.4030; *iso-Pr*, b_{745} 101-2°, n_D^{20} 1.3966, d_{20} 1.0777; *Bu*, b_{15} 40-7°, b_{756} 138°, n_D^{20} 1.4128, d_{20} 1.0513. $COCl_2$ with ROH in MePh in the presence of 5-8% quinoline gave the following $ClCO_2R$: *iso-Bu*, b_{750} 123-7°; *iso-Am*, b_{754} 150-1°, n_D^{20} 1.4176, d_{20} 1.0490; C_8H_{17}, b_3 86.5°, b_{10} 96-7°, b_{13} 107°, n_D^{20} 1.4330, d_{20} 0.9841; *cyclohexyl*, b_{21} 80-5°, n_D^{20} 1.4028; *l-menthyl*, b_8 96°, b_{11} 108-9°, n_D^{20} 1.4712; $PhCH_2$, b_7 85-7°; with an equimolar amt. of quinoline were obtained: *sec-Bu*, 72%, b_{23} 30-1°, b_{760} 121-1°, n_D^{20} 1.4490; *1-methyl-2-cyclohexyl*, b_{10} 101.6°, n_D^{20} 1.4560; *Ph*, b_7 64°, n_D^{20} 1.5162. The diamines (0.025 mole) in Et_2O were treated with 0.025 mole powd. potash, then 1.5-2 ml. H_2O, and RO_2CCl in Et_2O was added with cooling; the usual treatment gave the desired urethan derivs.: $Me_2NCH_2CH_2CH_2NHCO_2Et$, 55.8%, b_{15} 137-7°, n_D^{20} 1.4480, d_{20} 0.9853; *l-menthyl ester*, 51.8%, b_1 164.5°, n_D^{20} 1.4706, d_{20} 0.9557, m. 45°; $Et_2NCH_2CH_2CH_2NHCO_2Et$, 66.7%,

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b_3 130°, n_D^{20} 1.4503; *iso-Pr ester*, 53.9%, $b_{1.5}$ 123-3°, n_D^{20} 1.4452, n_D^{20} 1.4493, d_{20} 0.9307; *sec-Bu ester*, 42.5%, b_3 132°, n_D^{20} 1.4513, d_{20} 0.9334; *C_5H_{11} ester*, 63.3%, b_3 181.5-2°, n_D^{20} 1.4528, n_D^{20} 1.4577, d_{20} 0.0168; *cyclohexyl ester*, 46.5%, $b_{1.5}$ 105-7°, n_D^{20} 1.4725, n_D^{20} 1.4762, d_{20} 0.9765; *2-methylcyclohexyl ester*, 81.5%, b_3 177°, n_D^{20} 1.4683, n_D^{20} 1.4723, d_{20} 0.9079; *l-menthyl ester*, 88.2%, b_3 173°, n_D^{20} 1.4719, d_{20} 0.9482, m. 31°; *Ph ester*, 33.6%, b_3 199-201°, n_D^{20} 1.4770; *$PhCH_2$ ester*, 24%, b_3 132-5°, n_D^{20} 1.5030. *$C_4H_8NCH_2CH_2CH_2NHCO_2Et$*, 78.3%, b_3 150-3°, n_D^{20} 1.4742, d_{20} 1.0070; *Pr ester*, 70.4%, b_{14} 187-8°, n_D^{20} 1.4735, d_{20} 0.9935; *iso-Pr ester*, 62.8%, b_3 155-8°, n_D^{20} 1.4700, d_{20} 0.9878; *Bu ester*, 62.8%, b_3 146°, b_3 167-8°, n_D^{20} 1.4730, d_{20} 0.0788; *iso-Bu ester*, 53.5%, b_3 136.5-7°, n_D^{20} 1.4710, d_{20} 0.0813; *iso-Am ester*, 66.2%, b_3 159.5°, n_D^{20} 1.4712, d_{20} 0.9740; *C_5H_{11} ester*, 63.7%, b_3 212-13°, n_D^{20} 1.4720, d_{20} 0.9550.

G. M. Kosolapoff

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CA

Reaction of formamide with carbonyl compounds in the presence of nickel catalyst. A. N. Kost, A. P. Terent'ev, and G. A. Shvekhgeimer (Moscow State Univ.). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1951, 150-60.—The reaction of HCO_2NH_4 with carbonyl compds. is accelerated by the presence of hydrogenation catalysts (Ni, Co, Pt, Pd, etc.), and the limit of active temp. is lowered by 20-80°. Particularly effective are such substances in reactions of naphthenic compds. The use of catalysts improves the yield of primary amines. The results indicate that the mechanism of the reaction is such the H_2O-removing substances have little bearing on it and the true mechanism may proceed by addn. of $HOCNH_2$ to R_2CO in the sense of addn. of the HOC and NH_2 (or NR_2) fragments across the CO link of the carbonyl; the resulting $R_2C(NH_2$ or $NR_2)OCHO$ then decomp. into CO_2 and the amine R_2CHNH_2 (or NR_2). The above mentioned catalysts give 2-5% better yields of RNH_2 at 110-30° in comparison with the 180° required without a catalyst. The Ni catalyst was prepd. by treating Ni carbonate with excess HCO_2H 10-12 hrs. at room temp., filtering the Ni formate, and thermally decompg. the requisite amt. just before use after moistening with a little HCO_2H; the decompn. was done by an ordinary burner. Typical reactions with *HCO_2NH_4* (I) (from the reaction of 82% HCO_2H with $(NH_4)_2CO_3$, followed by concn.) follow. Heating 60 g. I, 1 g. Ni catalyst, and 24.5 g. MeEtCO 60 hrs. at 90° and 6 hrs. at 100°, then hydrolysis by boiling 2 hrs. with 100 ml. concd. HCl, gave 51.5% *2-aminobutane*, b_{760} 61-3°; *picrate*, m. 137-8°. Similarly 60 g. I and 30 g. MePrCO with 1 g. Ni gave 43.5% *2-aminopentane*, b_{760} 88-91°; *HCl salt*, m. 168° (from EtOH). To 60 g. I and 1 g. Ni in a Claisen flask heated to 130° was slowly (0.5 hr.) added 25 g. EtPrCO and the mixt. heated 7 hrs. at 125-30° with recycling of the distd. ketone, yielding 32.8% *3-aminohexane*, b_{760} 118-22°; *HCl salt*, m. 225°. Similarly MeAmCO gave 55.1% *2-aminoheptane*, b_{760} 140-3°; *HCl salt*, m. 183°; heating at 120-5° 4 hrs. gave a 49% yield. Similarly Pr_2CO after 8 hrs. at 140° gave 63.8% *4-aminoheptane*, b_{760} 138-41°; *HCl salt*, m. 240-1° (from EtOH); at 130-5° the yield is 64.4%, when the proportion of the ketone is higher. I (75 g.) and 48 g. $MeCOC_6H_{13}$ gave in 3 hrs. at 155-60° 59.4% *2-aminooctane*, b_{760} 164-7°; *HCl salt*, m. 83.5° (from EtOH). Heating 120 g. I, 2 g. Ni, and 84.2 g. iso-Pr_2CO

TERENT'YEV, A.P.; KOST, A.N.; GURVICH, S.M.

Condensation of acrylonitrile with some dienes. Vestnik Moskov. Univ. 6, No.12, Ser. Fiz.-Mat. i Estestven. Nauk No.8, 79-83 '51. (CA 47 no.14:6877 '53)

CA

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Syntheses with acrylonitrile. XII. Preparation of some analogs of spermine and spermidine. A. P. Terent'ev, A. N. Kost, and K. I. Chursina (Moscow State Univ.). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 21, 268-70(1951); cf. *C.A.* 44, 9340*f*; 45, 5022*e*.—To 14.8 g. $H_2N(CH_2)_3NH_2$ was added with cooling 10.6 g. CH_2:CHCN and the soln. warmed slowly to 40-5°, then 2 hrs. on a steam bath, and rapidly distd. in a N atm. to give 80% *$H_2N(CH_2)_3NH$-CH_2CH_2CN*, b$_3$ 200-10°, and about 3 g. dicyanoethylation product, b$_3$ 230-70°; when 2 moles CH_2:CHCN is used, 70% mono-(I) and 23% *dicyanoethylation* (II) products are formed. I, b$_3$ 203-6°, b$_4$ 214-18°, n_D^{20} 1.4762, d_4^{20} 0.9725, forms a cryst. *di-HCl salt*, darkening at 180°; II, *N,N'-bis(2-cyanoethyl)-1,3-propanediamine*, b$_3$ 263.5°, b$_4$ 271.5°, n_D^{20} 1.4826, d_4^{20} 1.0168. Reduction of 12.7 g. I by 15 g. Na added to a soln. in 250 ml. BuOH at 100° and steam distn. (125-35°) gave 82% *1,5-diazacyclooctane-2HCl.H_2O*, m. 270° (from aq. MeOH); *dipicrate monohydrate*, decomp. 226°. Similar reduction of II gave 72% *N,N'-bis(3-aminopropyl)ethylenediamine-4HCl.H_2O*, darkening at 150°, a *spermine homolog*. G. M. Kosolapoff

1951

KOST, A. N.

USSR/Chemistry - Polyamide Fibers
Vitamin B_1

Oct 51

"Synthesis With the Aid of the Nitrile of Acrylic Acid. XIV. Preparation of the Dinitrile of Succinic Acid," A. P. Terent'yev, A. N. Kost, Lab of Org Chem imeni Acad N. D. Zelinskiy, Moscow State U

"Zhur Obshch Khim" Vol XXI, No 10, pp 1867-1869

Describes prepn of dinitrile of succinic acid (yield 80-85%) by action of acrylonitrile on satd aq soln of KCN and $MgSO_4$. The dinitrile can serve as starting material for synthesis of vitamin B_1 or can be reduced to putrescine (starting material for synthesis of polyamide fibers and used in prepn of series of compds with high physiol activity, i. e., spermine. Results suggest use of mixt of KCN and $MgSO_4$ solns in many cases as substitute for hydrocyanic acid.

PA 194T35

KOST, A. N., YASHUNSKIY, V. G.

Chemists

A. N. Vyshnegradskiy. Vest. Mosk. un., 7, No. 2, 1952.

9. Monthly List of Russian Accessions, Library of Congress, October, 1952~~1953,~~ Unclassified.

KOST, A.N.

Preparation of 1-naphthylacetic acid. A. N. Kost. [redacted] *Vestnik Moskov. Univ.* 7, No. 12, Ser. Fiz.-M [redacted] Nauk No. 8, 35-7(1952).—To 380 g. $C_{10}H_8$, 10 g. Ac_2O, and 200 ml. petr. ether (b. 80-100°) was adde in 4 hrs. with cooling 300 g. $AlCl_3$, the mixt. stirred 6 hrs., kept overnight, and quenched with ice and 200 ml. cc ed. HCl. Extn. with C_6H_6 gave 88% $1\text{-}AcC_{10}H_7$, b_5 143-5°, contg. some 2-isomer. To 10 g. Mg was added 82.8 g. $1\text{-}C_{10}H_7Br$ in 250 ml. Et_2O and the resulting soln. of $1\text{-}C_{10}H$ MgBr was treated with 54.5 g. fresh powd. $ZnCl_2$, stirred hr., then treated with 31.2 g. AcCl in Et_2O; after 2 h , at room temp. the mixt. was treated with ice and 5% H SO_4, yielding 25% $C_{10}H_8$ and 70.6% *1-$C_{10}H_7Ac$*, b_{11} 101-2°, n^{20}_D 1.0222, d_{20} 1.1338. This (17 g.), 10 g. S, 50 ml. 30% a. NH_4OH, and 15 ml. pyridine were heated in autoclave -9 hrs. at 160-70°, treated with 100 ml. 40% NaOH, fluxed 6-8 hrs., extd. with C_6H_6, and the aq. layer aci fied, yielding 80% *1-naphthylacetic acid*, m. 154° (from H_2O).

G. M. Kosolapoff

KOST, A.N.

Chem Abs V48
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General + Physical
Chemistry

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Aleksei Nikolaevich Vyshnegradskii. A. N. Kost and V. G. Yashunskii. *Uspekhi Khim.* 21, 260-4(1952).—Brief summary of scientific work (1851-1880) of Vyshnegradskii with 22 references. G. M. Kosolapoff

AF
7-19-54

KOST, A.N.

Chem ③

Chemical Abst.
Vol. 48 No. 5
Mar. 10, 1954
Organic Chemistry

Syntheses with acrylonitrile. XV. Preparation of 3-phenyl- and 3,4-diphenylpiperidine. A. N. Kost and A. P. Terent'ev (Moscow State Univ.). *J. Gen. Chem. U.S.S.R.* 22, 719-21(1952)(Engl. translation).--See C.A. 47, 2759h.
H. L. H.

MF
7-13-54

Kost, A.N.

Syntheses with acrylonitrile. XVI. Mechanism of cyanoethylation reaction. A. P. Terent'ev, A. N. Kost, and S. M. Gurvich (Moscow State Univ.). ~~Zhur. Obshchei~~ *Khim.* 22, 1977-80(1952); cf. *C.A.* 47, 2759*h*.—The mechanism of the cyanoethylation reaction is discussed on an ionic basis which takes into account the normal polarization of acrylonitrile (I). The transcyanoethylation reaction is rather slow and requires heating; the rupture of the OC link occurs more readily than that of NC. $EtONMe_2Ph$ (II) in alc. is a very useful cyanoethylation catalyst (cf. Rodionov and Yartseva, *C.A.* 42, 4012*a*); in its prepn. it is necessary that no p-$MeC_6H_4SO_2Cl$ be present in the initial p-$MeC_6H_4SO_3Me$, since otherwise the product has a blue color and its activity is low. I and $PhCH_2CN$ do not react with II at 0-3°, but at 10-15° a violent reaction occurs; hence, II must be added first, followed by dropwise addn. of I. In a typical expt. 21 g. cyclopentanone in 250 ml. C_6H_6 and 1 ml. fresh II were treated dropwise with stirring and cooling at 25-30° over 3 hrs. with 58 g. I (if crystals form early, the addn. of I is interrupted, the mixt. warmed to 40° and 5-6 drops more II added), and the mixt. was stirred 3 hrs. at 40-50°, let stand overnight, and filtered, yielding 95-7% *2,2,5,5-tetrakis(2-cyanoethyl)cyclopentanone*, m. 175.5°; Triton B catalyst gave the same result. I with AcPh in C_6H_6 with II catalyst at 20° gave 95% $BzC(CH_2CH_2CN)_3$, m. 129-0.5°; Triton B in dioxane soln. at 30-40° gave a 67% yield and $BuONMe_2CH_2Ph$ catalyst (III) in Me_3COH at 20° a 64% yield. I and $PhCH_2CN$ with II in C_6H_6 at 25-30° gave 90% $PhC(CN)(CH_2CH_2CN)_2$, m. 71.5°; KOH in MeOH in Me_3COH solvent at 10-25° gave 70%. $AcCH_2CO_2Et$ with I in C_6H_6 and II catalyst at 20° gave 85% $AcC(CH_2CH_2CN)_2CO_2Et$, m. 83°; Triton B in dioxane at 20° gave 70% and III in dioxane gave 80%. Carbazole and I in C_6H_6 at 0° with II catalyst gave 89% *1-(2-cyanoethyl)carbazole*, m. 150.5°; Triton B gave 84.5%. *2-Phenylindole* and I with II catalyst in C_6H_6 at 60° gave 83% *1-(2-cyanoethyl) deriv.*, m. 88-90°; Triton B gave 80%. From 120 g. 40% aq. soln. of 1.3 moles Me_2NH treated gradually with 53 g. I and heated hrs. on a steam bath was obtained 73% $Me_2NCH_2CH_2CN$ (IV), b. 169-71°. IV (9.8 g.) and 15 g. piperidine heated 10 hrs. at 160° gave 30% $C_5H_{10}NCH_2CH_2CN$, b_4 77-8°, n_D^{20} 1.4705, d_{20} 0.9438; *picrate*, m. 158°. Similarly IV and Bu_2NH heated 40 hrs. at 170° gave 20% $Bu_2NCH_2CH_2CN$, b. 113-13°, n_D^{20} 1.4450, d_{20} 0.8604; *picrate*, m. 78°. Heating 8.5 g. $MeOCH_2CH_2CN$ and 8.5 g. piperidine 16 hrs. at 120° gave 13% $C_5H_{10}NCH_2CH_2CN$; similarly, Bu_2NH in 16 hrs. at 180° formed 15% $Bu_2NCH_2CH_2CN$. Na (2.3 g.) in 40 ml. abs. EtOH heated 10 hrs. on steam bath with 82 g. $CH_2(CO_2Et)_2$ and 9.9 g. $EtOCH_2CH_2CN$, and the mixt. dild. with 3 vols. H_2O, acidified with HCl, and extd. with Et_2O gave 27% $(EtO_2C)_2CHCH_2CH_2CN$, b_5 140-2°, n_D^{20} 1.4350, d_{20} 1.0881, and 10% $(EtO_2C)_2C(CH_2CH_2CN)_2$, b. 103-8°, m. 61° (from EtOH). Heating 4.3 g. $AcC(CH_2CH_2CN)_3$, 18 ml. dry Me_2CO, and 0.5 g. solid KOH in an ampule 1 hrs. at 100° or 6 hrs. at 150° yielded no condensation product. Na (0.5 g.) in 25 ml. abs. EtOH and 3 g. $AcC(CH_2CH_2CN)_3$ refluxed 7 hrs. and the mixt. acidified with AcOH and distd. gave only the starting material; a similar reaction at 200° over solid KOH employing the vapor of MeOH also gave a neg. result. $AcC(CH_2CH_2CN)_3$ refluxed hrs. with Et_2NH did not react.

G. M. Kosolapoff

KOST, A. N., YASHUNSKIY, V. G.

Propionitriles, Vvshnegradskiy Reaction

Anomalous behavior of β-substituted propionitriles
in the Vyshnegradskii reaction. Dokl. AN SSSR 83 no. 1, 1952

SO: Monthly List of Russian Accessions, Library of Congress, August 195~~1~~2, Uncl.

Kost, A.N.

USSR.

The acetylation of amines and hydrazines with vinyl acetate. A. N. Kost and A. M. Yurkevich. *Vestnik Moskov. Univ.* 8, No. 2, *Ser. Fiz.-Mat. i Estestven. Nauk* No. 1, 69-75(1953).—Hagemeyer, Jr., and Hull (*C.A.* 44, 2917*c*) showed that AcOC(:CH_2)Me (I) is a mild acetylating agent. The authors investigated the action of AcOCH:CH_2 (II) on amines (III) (*C.A.* 45, 10194*e*) and hydrazines (IV) and found that II is more active than I. With III and IV, I gives their Ac derivs. and AcH. The side products are polymers of II and IV hydrazones. III of the aliphatic and cyclohexane series react readily, often with spontaneous heat evolution and give good yields. The branched III react more slowly and give lower yields. PhNHEt and Ph_2NH do not react either at room temp. or on a water bath or on adding HCl. The authors used II distd. over Na, b_{760} 72-4°, n_D^{20} 1.3958. The amt. was mostly in equimolecular amt. The following compds. are described [S = spontaneous heat evolution; length of heating (on water bath unless otherwise stated), and % yield given]: MeCH(NHAc)-CH_2CH_2Me, S, 1 hr., 63%, b_{745} 224-6°; $AcNHCH_2CH_2OH$, 30 min., 78%; $Me_2CCH(NHAc)Me$, 2 hrs., 80%, b_{14} 100-2°, m. 68° (90% by heating on a gauze with 1.25-fold excess of II); PhCH(NHAc)Et, 2 hrs. at 30-40° with 2-fold excess of II, 64%, b_6 155-6°, m. 75-5.5°; $C_6H_{11}NHAc$, 1 hr. at 30-40°, 71%; 3-amino-1-methylcyclohexane S, 2 hrs., 85%;

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OVER

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Dimethylaminomethylation of 2-naphthol. N. A. Dzbanovskii, S. V. Marochko, and A. N. Kost (Moscow State Univ.). *Sbornik Statei Obshchei Khim., Akad. Nauk S.S.S.R.* 1, 607-9(1953).—To 200 g. 60% aq. Me_2NH at 0° was added over 1.5 hrs. 100 g. 35% formalin and the sirup treated with 200 g. K_2CO_3; distn. of the org. layer gave 69% *$CH_2(NMe_2)_2$*, b. 80-5°, (I). To 73 g. I was added with stirring 102 g. 2-$C_{10}H_7OH$ and the mixture heated 2.5 hrs. to 75-80°, cooled, taken up in 200 ml. 13% HCl, filtered, and treated with 28 g. NaOH in 150 ml. H_2O to yield a ppt. of 127 g. *1-dimethylaminomethyl-2-naphthol* (II), m. 74-5°; 93% with recovery from the soln. To 21 g. I was added 60 g. 80% aq. AcOH and the soln. added to 28.8 g. 2-$C_{10}H_7OH$, the mixt. allowed to stand overnight and treated with NaOH, gave 90% II. To 40 g. 60% aq. Me_2NH at 0° was added cold 31 g. 35% formalin; after 1 hr. at room temp. the mixt. was added to 30 g. 2-$C_{10}H_7OH$, allowed to stand 4 hrs., the ppt. sepd., taken up in 10% HCl and treated with NaOH as above, yielding 80-3% II. To 23 g. 50% aq. Me_2NH at 0° was added 21 g. 35% formalin and the mixt. poured into 30 g. 2-$C_{10}H_7OH$ (temp. rise to 40-50°) to yield a coagulated product, which purified as above gave 70% II. To 50 g. 80% AcOH was added with cooling 75 g. 30% Me_2NH, followed by 42 g. 35% formalin, and the soln. treated at room temp. with 72 g. 2-$C_{10}H_7OH$ and heated to 70° gave after a total heating of 1 hr. (5 min. at 100°) 100 g. resinous mass which was generally insol.

G. M. Kosolapoff

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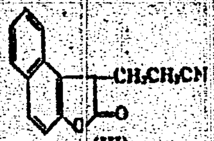
Reactions of mobile amino group. I. Reactions of substitution of the dimethylamino group in 1-(dimethylaminomethyl)-2-hydroxynaphthalene. A. P. Terent'ev, A. N. Kost, N. A. Dzbanovskii, and S. V. Marochko (Moscow State Univ.). *Sbornik Statei Obshchei Khim., Akad. Nauk S.S.S.R.* 1, 610-15(1953); cf. preceding abstr.—1-(Dimethylaminomethyl)-2-hydroxynaphthalene (68 g.) in 260 ml. EtOH with 37.5 g. KCN in 85 ml. H_2O heated in an autoclave 6.5 hrs. at 180-200° gave on cooling a brown ppt. of K *1-(2-hydroxynaphthyl)acetate*, in 75% yield; washing with EtOH, soln. in 2% NaOH, and pptn. with HCl gave 63% *free acid* (I), m. 1[illegible]° (from H_2O). I treated with Me_2SO_4 in 10% NaOH at [illegible]0-100° gave [illegible]% *1-(2-methoxynaphthyl)acetic acid*, m. 21[illegible]° (from EtOH), while I with BzCl in 10% NaOH gave 4[illegible]% *1-(2-benzyloxynaphthyl)acetic acid*, m. 165.5-7° (from MeOH). I (15 g.) and 30 g. Ac_2O refluxed 13 hrs. gave 60% *lactone* (II), m. 103°. II (1.8 g.) in dioxane treated with 0.06 g. KOH in abs. EtOH followed by 1.0 g. $CH_2:CHCN$, and refluxed 2 hrs., gave 20% III, m. 91° (from H_2O). Me_2SO_4 added slowly (13.2 g.) to 20 g. 1-(dimethylaminomethyl)-2-hydroxynaphthalene in 50 ml. EtOH, the resulting soln. added over 1 hr. to 50.5 g. cryst. Na_2SO_3 in 60 ml. H_2O at 80°, heated 2 hrs. and cooled, yielded 81% *1-(2-hydroxynaphthyl)methanesulfonic acid*, plates (from dil. EtOH), *S-benzylthiuronium salt* (IV), m. 224-7°. IV is formed in 72% yield when 50.5 g. cryst. Na_2SO_3, 8.6 g. 35% formalin, and 20 ml. H_2O are treated with 14.4 g. 2-$C_{10}H_7OH$, heated 4 hrs. at 80-90°, filtered and acidified with H_2SO_4. $CH_2(CO_2Et)_2$ ([illegible] g.) was added to 7 g. Na in 100 ml. EtOH, followed by slow addn. of 20 g. 1-(dimethylaminomethyl)-2-hydroxynaphthalene and 130 g.



(III)

Kost A.N.

USSR.

Some derivatives of thiodipropionic acid. A. N. Kost, I. A. Lebedev, and V. G. Yashunskii. *Vestnik Moskov. Univ.* 8, No. 3, *Ser. Fiz.-Mat. i Estestven. Nauk* No. 2, 111-14(1953).—Treating $Na_2S.9H_2O$ (1 mole) with 2 moles $CH_2:CHCN$ dropwise at 15-17°, stirring 4 hrs. at room temp., gave an oily layer which, when extd. with C_6H_6, washed, dried, and distd. yielded 8[illegible]-0% β,β'-dicyanodiethyl sulfide (I), needles, m. 26°, $b_{1.5-1}$ 163-4°, n_D^{20} 1.5047, d_{20} 1.1270. Considerably lower conversions were obtained at faster reaction rates or higher temps. Refluxing I (0.143 mole) 4 hrs. with 100 ml. concd. HCl yielded 90% β,β'-thiodipropionic acid (II), m. 133.5° (from H_2O). The following derivs. of II were obtained by conventional methods: di-Et ester, b_7 148°, n_D^{20} 1.4646, d_{20} 1.0051; di-Bu ester b_{11-12} 194.6°, n_D^{20} 1.4647, d_{20} 1.0326; dianilide, m. 162.5° (from EtOH); di-p-toluidide, m. 108.5° (from EtOH).

Gerard Auflegger

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Sulfonation of enol acetates. A. P. Terent'ev, A. N. Kost, A. M. Yurkevich, E. E. Khaskina, and L. I. Obreimova. *Vestnik Moskov. Univ.* 8, No. 6, *Ser. Fiz.-Mat. i Estestven. Nauk* No. 4, 121-4(1953); cf. *C.A.* 44, 1095g.—To 2.3 g. of vinyl acetate (I) was added 5 g. of pyridine-SO_3 complex in 10 cc. $(CH_2Cl)_2$. After heating 8 hrs. at 120° the mixt. dissolved in hot H_2O, treated with 0.5 cc. of 0.2*N* H_2SO_4, refluxed 4 hrs., AcOH distd. off and the soln. treated with $BaCO_3$ gave 85% $(OHCCH_2SO_3)_2Ba$ (II) (from MeOH). Since intermediate product $AcOCH:CHSO_3Ba/2$ (presence indicated by decolorizing $Br-H_2O$) hydrolyzed readily in acid to give AcOH it was desirable to carry out the hydrolysis rapidly. The same type of sulfonation was carried out with isocrotyl acetate. After 10 hrs. at 150° in a sealed tube it gave 35% $[Me_2C(CHO)SO_3]_2Ba$. To a stirred soln. of 8 g. SO_3 in 50 cc. $(CH_2Cl)_2$ at 0°, was added 8.8 g. of dioxane and 4.3 g. of I, kept cold 6 hrs., then evapd. on a water bath 8 hrs., 5 cc. H_2O in 2 portions added, and treated with $BaCO_3$ to yield 20% II. To a similar dioxane-SO_3 iced mixt. 1 g. of isopropenyl acetate was added with stirring to yield 67% of $(C_3H_5O_4S)_2Ba.H_2O$. $ClHgCH_2CHO$ (*C.A.* 44, 7225*d*) was sulfonated with SO_3 in $(CH_2Cl)_2$ to give 41% $(HO_2CCH_2SO_3)_2Ba$ instead of the expected II, which in acid gave off CO_2 and did not form insol. salts with *S*-(β-naphthyl)thiuronium chloride (III). To 21.2 g. of I was added while cooling, 63 g. of dioxane dibromide in portions (cf. *C.A.* 44, 8354*e*), the lower layer washed with ice H_2O, dried over $CaCl_2$, distd. *in vacuo* gave $AcOCHBrCH_2Br$ (IV) (yield 50%), b_{13} 101-3°, n^{20}_{D} 1.5057, d_{20} 1.9170 (cf. McElvain, *C.A.* 39, 2500^9). To 2.5 g. IV was added 3 g. Na_2SO_3 in 25 ml. H_2O, heated under reflux and then treated in the usual manner with $BaCO_3$; after cooling, III was added and the salt recrystd. from C_6H_6, m. 202-3°. Identification of the sulfoaldehydes was simplified by the fact that the salts with III had a definite m.p. at 202-4°.

I. Bencowitz

B2

KOST, A. N.; YASHUNSKIY, V. G.

Nitriles

Anomalous reduction of -substituted propionitriles, according to Vyshnegradskiy. Zhur. ob. khim. 23, No. 2, 1953.

SO: Monthly List of Russian Accessions, Library of Congress, June 1953, Uncl.

KOST, A.N.

Reaction of mobile amino group II. Exchange of amino group in 3-(dialkylamino)propionitriles. A. P. Terent'ev, A. N. Kost, and S. M. Gurvich (Moscow State Univ.). *Zhur. Obshchei Khim.* 23, 615-17(1953); cf. *C.A.* 47, 8003*h*. —Slow addn. of Me_2SO_4 to $Me_2NCH_2CH_2CN$ in C_6H_6 gave the quaternary salt (I), needles (from MeOH), which, heated to 120°, begins to decomp. (at 200° the reaction is rapid) into $CH_2:CHCN$ and Me_3N. The former is obtained in 70% yield. Similar pyrolysis of the Et_2SO_4 salt at 180-200° gave 80% $CH_2:CHCN$ and a very low yield of $MeEt_2N$, b. 66-9° (picrate, m. 184°). Pyrolysis in the presence of solid KOH at 100-200° gave 88% $CH_2:CHCN$. Addn. of 44.9 g. $ClCH_2CH_2CN$ dropwise to 28 g. KOH and 10 g. Et_3N heated to 120° gave a distillate contg. 75-80% $CH_2:CHCN$. I (22 g.) refluxed 4 hrs. with 4.6 g. Na dissolved in 60 ml. MeOH gave Me_3N and 21% $MeOCH_2CH_2CN$, b_{760} 164-5°, n^{20}_D 1.4031, d_{20} 0.9488. Refluxing 24 g. $Me_2NCH_2CH_2CN.MeI$ with 5.6 g. KOH in 74 g. BuOH 6 hrs. gave 73.7% $BuOCH_2CH_2CN$, b_{10} 80-2°, d_{20} 0.8004, n^{20}_D 1.4174. Heating 13.4 g. $Et_2NCH_2CH_2CN.MeI$ with 4.8 g. KCN in 50 ml. H_2O in an autoclave 6 hrs. at 150-60° gave, after acidification of the cooled mixt. and extn. with Et_2O, 80% $(CH_2CO_2H)_2$, m. 182°.

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Chemical Abst.
Vol. 48
Apr. 10, 1954
Organic Chemistry

Syntheses with the aid of acrylonitrile. XIX. Reduction of acrylonitrile by the Vyshnegradskii method. V. G. Yashunskii, A. N. Kost, and A. P. Terent'ev (Moscow State Univ.). [illegible] *Khim.* 23, 753-6(1953); cf. *C.A.* 47, 8663b; 48, 2569i.—To 5.3 g. $CH_2{:}CHCN$ in 150 refluxing ml. abs. EtOH was added over 20 min. 15 g. Na, the mixt. was dild. with 100 ml. H_2O after completion of the reaction, steam-distd. into 10% HCl, and the steam distillate further treated with steam and evapd., yielding an oil which, with NaOH under Et_2O, gave 30% $EtOCH_2CH_2CH_2NH_2$, b. 49-50°. To 22 g. Na in 50 ml. hot MePh was added in 0.5 hr. 5.3 g. $CH_2{:}CHCN$ in 350 ml. iso-BuOH at 140-50°, then 200 ml. H_2O after soln. of the Na, and the product steam-distd. as above, yielding 63.1% iso-$BuOCH_2CH_2CH_2NH_2$, b_{14} 72-3°, and 1.28 g. $PrNH_2.HCl$, m. 160°. A similar reaction in BuOH gave 44.3% $BuOCH_2CH_2CH_2NH_2$, b_{23} 78-9°, b_{17} 71-2°; a lesser proportion of $CH_2{:}CHCN$ gave a 59.6% yield. Similarly was formed 41.4% iso-$AmOCH_2CH_2CH_2NH_2$, b_{23} 78.5-80.0°.

G. M. Kosolapoff

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Chemical Abst.
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Apr. 25, 1954
Organic Chemistry

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Sulfonation and sulfonic acids of acidophobic substances. XXII. Sulfonation of vinyl ethers. A. P. Terent'ev, A. N. Kost, A. M. Yurkevich, and E. E. Khaskina (Moscow State Univ.). *Zhur. Obshchei Khim.* 23, 746-53(1953); cf. *C.A.* 48, 3330*b*.—Heating 5 g. 25% soln. of CH_2:CHCl in $(CH_2Cl)_2$ and 6 g. pyridine-SO_3 in an ampul 1.5-2 hrs. at 170°, soln. in H_2O, neutralization with $BaCO_3$, steam distn. of the pyridine, filtration of the residue, treatment of the filtrate with C, concn., addn. of MeOH, and extn. of the product with hot EtOH for 3 days gave 5% ($HCOCH_2SO_3)_2Ba$ (I), formed apparently from the primary product $\overline{CH_2.CHCl.O.SO_2.O.Ba.O.SO_2}$. Similar reaction of Me_2C:CHBr gave after 6 hrs. at 110° 85% *Ba salt* of *3-sulfoisobutyraldehyde* (II), which reduces ammoniacal $AgNO_3$; *Pb salt*, sirup; *Ag salt*, insol. in H_2O. CH_2:CHOBu (2 g.), 3.2 g. pyridine-SO_3 and 6 ml. $(CH_2Cl)_2$ heated 9 hrs. at 70-90° and treated as above, gave 30% I, forming a *monohydrate* on crystn. from H_2O; refluxing the reactants 14 hrs. gives a 32.5% yield; use of dioxane-SO_3 gives 42%. I with *S*-2-naphthylthiuronium chloride gave the *S-2-naphthylthiuronium salt*, m. 202-4° (from C_6H_6). CH_2:CHOAc and pyridine-SO_3 in $(CH_2Cl)_2$ gave, after 8 hrs. at 120° and the usual treatment, 81% I; dioxane-SO_3 gave 62%. For better isolation of the product and removal of AcOH the product is best refluxed 1 hrs. with 0.2*N* H_2SO_4 before treatment with $BaCO_3$. H_2C:CMeOAc (1 g.) added to 1 g. SO_3, 6 ml. $(CH_2Cl)_2$, and 0.9 g. dioxane with ice cooling gave 67% *Ba acetonesulfonate monohydrate*. Refluxing 28.8 g. iso-PrCHO, 61 g. Ac_2O and 6 g. KOAc 10 hrs. gave 36.5 g. *Me_2C:CHOAc*, b_{750} 121-4°, n_D^{20} 1.4106, which, heated with pyridine-SO_3 10 hrs. at 150° in an ampul, gave 35% II. $ClHgCH_2CHO$ heated with SO_3 in $(CH_2Cl)_2$ 12 hrs. on a steam bath, treated with H_2O, freed of Hg salts with H_2S, and neutralized with $BaCO_3$, gave 41% *Ba sulfoacetate monohydrate* (from H_2O). Addn. of dioxane dibromide (62 g.) to 21.2 g. CH_2:CHOAc with cooling gave 50% *$BrCH_2CHBrOAc$*, b_{11} 101-3°, n_D^{20} 1.5057, d_{20} 1.0170, which (2.5 g.) refluxed 1 hr. with 3 g. Na_2SO_3 in 25 ml. H_2O, concd., treated with $BaCO_3$, filtered, evapd. and treated with S-2-

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KOST, A.N.

Acylation by means of vinyl acetate. A. N. Kost and A. M. Yurkevich (Moscow State Univ.). [redacted] Khim. 23, 1738-43(1953).—$CH_2:CHOAc$ (I) can be used as an acylating agent for alcs. in both acid and alk. mediums. Heating 6 g. iso-PrOH, 8.6 g. I, and 4 drops H_2SO_4 8 hrs. at 100-10° yielded propene and 4 g. iso-PrOAc, b_{760} 87.5-88°, n_D^{20} 1.3715, d_{20} 0.8740, for 39% yield. Similarly 8.8 g. $EtMe_2COH$ and 8.6 g. I gave 42% *$EtCMe_2OAc$*, b_{760} 124-5°, n_D^{20} 1.4010, d_{20} 0.8740. Allyl alc. (11.6 g.), 27.2 g. I, and 5-6 drops H_2SO_4 similarly gave 22% $CH_2:CHCH_2OAc$, b_{760} 102-3°, n_D^{20} 1.4043, d_{20} 0.9372; addn. of I to $CH_2:CHCH_2ONa$ even at 0° yields tarry resinous products and the ester could not be isolated. *n*-Hexanol (10.3 g.) and 8.0 g. I with a little H_2SO_4 similarly gave 49% $C_6H_{13}OAc$ (4.1 g. ROH was recovered), but with excess I the yield rises to 69%; the product, b_{760} 169-70°, n_D^{20} 1.4115, d_{20} 0.8770. Heating 10.3 g. *n*-hexanol and 8.0 g. I with 0.3 g. dry $Al_2(SO_4)_3$ in a sealed tube 20 hrs. at 100-5° gave 3 g. AcH and 54% $C_6H_{13}OAc$; $Al(OEt)_3$ catalyst in a similar reaction gave but 12% yield of the ester. 3-Hexanol (9 g.) and 7.7 g. I with 5-6 drops H_2SO_4 heated 8 hrs. at 100-10° gave 47% *EtPrCHOAc*, b_{760} 149-50°, n_D^{20} 1.4011, d_{20} 0.8870; 3.6 g. ROH was recovered; on addn. of I to RONa much heat was evolved but no ester was isolated. To 2.3 g. Na in 20 g. cyclohexanol was added at 0° 17.2 g. I; after diln. with Et_2O and sepn. of a ppt., the org. layer yielded 40.5% $C_6H_{11}OAc$, b_{760} 96-7°, n_D^{20} 1.4432, d_{20} 0.9664; a 35% yield (63% if the recovered alc. is considered) was obtained from 10 g. alc. 8.6 g. I, and 5-8 drops H_2SO_4 heated 8 hrs. at 100-10°; the product, b_{21} 98-100°, n_D^{20} 1.4435, d_{20} 0.9[illegible]. *1-Ethoxy-2-propanol* (10.4 g.) and 8.5 g. I with 6 drops H_2SO_4 heated as above gave 0.1 g. ROH and 35% corresponding acetate, b_{760} 184-5°, n_D^{20} 1.40[illegible]1, d_{20} 0.9456. Na (1.1 g.) in 12.2 g. $PhCH_2CH_2OH$ treated at 0° with 8.6 g. and the mixt. dild. with Et_2O gave 18% $PhCH_2CH_2OAc$, b_{12} 110-11°, n_D^{20} 1.5115, d_{20} 1.0341. Similarly furfuryl alc. gave 80% acetate, b_{21} 83-5°, n_D^{20} 1.4[illegible]02, d_{20} 1.1177. I (34.4 g.), 24.4 g. BzOH, 0.4 g. $Hg(OAc)_2$ and 3 drops H_2SO_4 heated 24 hrs. at 45-50°, 20 g. Na_2CO_3 and 80 ml. cold H_2O added, and the org. layer distd. gave 41% $CH_2:CHOBz$, b_{14} 98-100°, n_D^{20} 1.5282, d_{20} 1.0583. Similarly $PrCO_2H$ gave 51% $CH_2:CHO_2CPr$, b_{760} 115-16°, n_D^{20} 1.4006, d_{20} 0.9008. Heating 9.3 g. $PhNH_2$ and 3.7 g. $CH_2:CHOBz$ with 3 drops H_2SO_4 0.5 hr. at 100-20°, followed by washing with aq. HCl, gave 71% PhNHBz, m. 160-1°. Similarly, $PhNH_2$ and $CH_2:CHO_2CPr$, but without H_2SO_4, gave 85% PrCONHPh, m. 92°. It is pointed out that in reactions of I with nucleophilic agents such as amines, the initial reaction is an attack on the carbonyl C, followed by stabilization of the complex by migration of H ion and cleavage of AcH, the ease of acetylation being detd. largely by the nucleophilic nature of the reagent rather than by mobility of the H atom. Since alcs. show decreased nucleophilic character because of H-bonding assocn., the destruction of such assocn. is necessary before acylation. G. M. K.

Kost, A.N.

FD-1511

USSR/Chemistry

Card 1/1 : Pub. 129-14/18

Author : Kost, A. N.; Kamernitskiy, A. V.; Gurvich, S. M.

Title : Synthesis of 2,2-pentamethylenepyrolydine

Periodical : Vest. Mosk. un., Ser. fizikomat i yest. nauk, 9, No 6, 115-118, Sep 54

Abstract : Describes synthesis of the above new spirane. Synthesis consists of reducing the cyanoethylated nitrocyclohexane. Gives a convenient method for the preparation of gamma,gamma-dicyanopimelonitrile. Eight references (Three USSR)

Institution : Chair of Organic Chemistry

Submitted : January 7, 1954

TERENT'YEV, A.P.; KOST, A.N.; TSUKERMAN, A.M.; POTAPOV. V.M.;
SERGEYEV, P.G., professor, redaktor; STRUCHKOV, Yu.T.,
redaktor; MOSKVICHEVA, N.I., tekhnicheskiy redaktor.

[Nomenclature of organic compounds; survey, criticism, proposals] Nomenklatura organicheskikh soedinenii; obzor, kritika, predlozhenia. Moskva, Izd-vo Akademii nauk SSSR, 1955. 302 p. (MLRA 8:12)
(Chemistry, Organic--Nomenclature)

Kost, A.N.

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Systematic nomenclature of organic compounds. A. P. Terent'ev, V. M. Potapov, A. N. Kost, and A. M. Tsukerman. *Vestnik Moskov. Univ.* 10, No. 6, *Ser. Fiz.-Mat. Estestven. Nauk* No. 4, 97-134(1955).—A new general system of nomenclature is proposed applicable to the naming of customary compounds consideration of geometric and optical isomers is given. John Howe Scott

USSR/Chemistry - Nomenclature FD-1683

Kost, A.N.

Card 1/1 : Pub. 129-8/25

Author : Terent'yev, A. P.; Kost, A. N.; Tsukerman, A. M.

Title : A new system of numbering atoms in condensed cyclic structures

Periodical : Vest. Mosk. un., Ser. fizikomat. i yest. nauk, Vol. 10 69-76. Feb 1955

Abstract : Proposes a new system for numbering condensed cyclic molecules which depends on the structure of the compound and therefore can be used for both carbo- and heterocyclic structures. The atoms in the condensed cyclic structures are divided into four classes depending on whether they are non-junctional, junctional, junctional with three structural atoms, or junctional with four structural atoms. Diagrams; eight references (one USSR).

Institution : Chair of Organic Chemistry

Submitted : April 14, 1954

KOST, A.N.; YERSHOV, V.V.

Reactions of hydrazine derivatives. Part 3. 3-aryl-pyrazolines.
Vest.Mosk. un.10 no.12:115-117 D '55. (MLRA 9:5)

1. Kafedra organicheskoy khimii.
(Hydrazine) (Pyrazoline)

GRANDBERG, I.I.; KOST, A.N.

Reactions of hydrazine derivatives. Part 4. New synthesis of benzylhydrazine. Vest.Mosk. un.10 no.12:119-120 D '55.
(MLRA 9:5)

1. Kafedra organicheskoy khimii.
(Hydrazine)

Kost, A. N.

Reaction of vinyl ethers with amines. A. N. Kost, A. M. Yurkevich, L. G. Yudin, and T. A. Shchegoleva (Moscow State Univ.). *Zhur. Obshchei Khim.* 25, 943-7(1955); *J. Gen. Chem. U.S.S.R.* 25, 907-10(1955)(Engl. translation); cf. *C.A.* 48, 13622e.—Syntheses of 2-methylquinolines from vinyl ethers and amines are described. To 9.3 g. PhNH$_2$ and 0.2 g. PhNH$_2$.HCl was added dropwise at 95-100° 5 g. BuOCH:CH$_2$ and the mixt. heated gradually to 130° over 4 hrs. Distn. gave 2.7 g. quinaldine, b$_4$ 84-90° (picrate, m. 190-1°), contg. traces of PhNH$_2$. The same yield resulted after 25 days in sealed tube at room temp. When a trace of Bz$_2$O$_2$ was used instead of PhNH$_2$.HCl, the yield was 34%; BF$_3$.Et$_2$O catalyst gave 30% yield. When 18.6 g. PhNH$_2$, 10 g. BuOCH:CH$_2$, 0.5 g. PhNH$_2$.HCl, and 40 ml. xylene were heated 25 hrs. on a steam bath, then acidified, steam distd. to remove the solvent and BuOH, and the residue made alk. and steam distd. again, there was obtained 43% quinaldine; if the purification is made with Ac$_2$O, the yield rises to 57%; purification with ZnCl$_2$ gives 38% yield. Dioxane instead of xylene gave the same yield, but without the solvent the yield reaches only 33%. PhNH$_2$ and EtOCH:CH$_2$ gave 30% quinaldine; PhNH$_2$ and iso-BuOCH:CH$_2$ gave 31% quinaldine. Heating 21.4 g. *p*-MeC$_6$H$_4$NH$_2$, 10 g. BuOCH:CH$_2$, and 0.5 g. *p*-MeC$_6$H$_4$NH$_2$.HCl in sealed tube 20 hrs. at 100° gave 74% crude 2,6-dimethylquinoline, or 51% pure product, b$_4$ 106-7°, m. 59.5°; purification with Ac$_2$O instead of steam distn. gave 54% yield. Dioxane tends to raise the yield; the use of EtOCH:CH$_2$ gave a 35% yield. Heating 21.4 g. *o*-MeC$_6$H$_4$NH$_2$, 10 g. BuOCH:CH$_2$, and 0.5 g. *o*-MeC$_6$H$_4$NH$_2$.HCl in 50 ml. dioxane 25 hrs. at reflux gave 63% 2,8-dimethylquinoline; purification with PhSO$_2$Cl gave 44% pure product, while the use of Ac$_2$O gave 58%; pure product, b$_4$ 103-4° (picrate, m. 180-1°). To 12.3 g. *p*-MeOC$_6$H$_4$NH$_2$, 0.5 g. of its HCl salt, and 50 ml. dioxane was added slowly at reflux over 2 hrs. 10 g. BuOCH:CH$_2$ and the mixt. refluxed 16-18 hrs. to give 15% 2-methyl-6-methoxyquinoline, b$_4$ 120-3°, m. 67°; at 80° the yield dropped to 7%; without dioxane no reaction took place. Similarly 2-C$_{10}$H$_7$NH$_2$ yielded after 25 hrs. at 100° 29% *2-methyl-5,6-benzoquinoline*, m. 81-2° (*picrate*, m. 221°), if an equimolar proportion of reactants is used; a 2:1 molar ratio gave 7% yield. Refluxing 10.9 g. *o*-H$_2$NC$_6$H$_4$OH, 20 g. BuOCH:CH$_2$, 30 ml. dioxane, and 0.6 g. PhNH$_2$.HCl 20 hrs. gave 10% *8-hydroxyquinaldine*, m. 70° (crude, m. 74° (after sublimation). Mixing 9.3 g. PhNH$_2$, 10 g. BuOCH:CH$_2$, 8.8 g. pyruvic acid, 40 ml. abs. EtOH, and 0.5 g. PhNH$_2$.HCl resulted in vigorous reaction, which required cooling; after refluxing 10 hrs. the mixture yielded 20% *2-methylcinchoninic acid*, m. 240-1° (*picrate*, m. 189-90°) [cf. Doebner, *Ber.* 20, 277(1887)]. G. M. Kosolapoff

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Kost A.N.

Catalysts and mechanism of the Leuckart reaction. A. N. Kost and I. I. Grandberg (Moscow State Univ.). *Zhur. Obshchei Khim.* 25, 1432-7(1955).—Alk. catalysts in the presence of Raney Ni accelerate the Leuckart reaction and direct the reaction to the formation of predominant formation of secondary amines. It was shown that the Leuckart reaction goes through the step of dissocn. of HCONH$_2$, and the 1st product is not the amine but its formyl deriv. Improved techniques for formation of amines are described below. To 450 g. mixt. contg. 6 moles HCONH$_2$ and 2.5 moles HCO$_2$H (prepd. by passing NH$_3$ into 85% HCO$_2$H or addn. of (NH$_4$)$_2$CO$_3$ to the acid, followed by distn. to bath temp. 150°; the residue was heated until the pot temp. rose to 175-80°, when the mixt. was distd. *in vacuo* to yield HCONH$_2$], was added 1 g. Raney Ni, the mixt. heated to 120° and treated over 1.5 hrs., with continuous distn., with 150 g. cyclohexanone; after 1.5 hrs. further heating the mixt. was treated with 300 ml. 50% NaOH, decanted, and the ppt. treated with hot H$_2$O; the sepd. oil was taken up in Et$_2$O and distd., yielding 98% *formylcyclohexylamine*, b$_{11}$ 153-4°, b$_{753}$ 268-74°, m. 27°, n_D^{20} 1.4892, d$_{20}$ 1.0123. To 100 g. formate-formamide mixt. was added 100 g. 85% HCO$_2$H and 0.5 g. Raney Ni, followed at reflux over 1.5 hrs. by 48 g. cyclohexanone; after 2.5 hrs. at 115°, evapn. with 500 ml. concd. HCl, treatment with KOH and distn. there was obtained 85.2% cyclohexylamine, isolated as the HCl salt, m. 207°. CO(NH$_2$)$_2$ (30 g.), 29.4 g. cyclohexanone, 20 g. 85% HCO$_2$H, and 0.5 g. Raney Ni heated 3 hrs. to 110° while 20 g. HCO$_2$H was being added, gave 84.8% dicyclohexylamine, b$_{11}$ 137-9° (HCl salt, m. 335°). To a refluxing mixt. of 18.5 g. HCONH$_2$, 47.7 g. Ac$_2$O, and 0.5 g. Raney Ni was added over 20 min. 0.9 g. cyclohexylamine, heated 40 min. and treated with NaOH yielding 74% *acetylcyclohexylamine*, m. 102-3°; no formylcyclohexylamine was detected. If Ac$_2$O is omitted, the formyl deriv. formed in 32% yield. This with Na under Et$_2$O gave a powdery Na enolate of the formylcyclohexylamine, which with EtI gave 22.8% *ethylcyclohexylamine*, b$_{754}$ 163-5° (picrate, m. 132°), after the sapon. of the intermediate formyl deriv. with 5% NaOH at reflux. In the Leuckart reaction the addn. of the ketone component to the hot HCONH$_2$ tends to raise the yield of the primary amine. If HCONH$_2$-HCO$_2$H is added to excess ketone, the secondary amine is mainly formed but part of the ketone is unreacted. Addn. of Ni facilitates the reaction by accelerated decompn. of HCO$_2$H and decline of acidity of the medium. In a basic soln. (pyridine, NH$_3$, Na or urea salts) the reaction goes very energetically. Excess acid almost prevents the formation of secondary amine. Also in *J. Gen. Chem. U.S.S.R.* 25, 1377-81(1955)(Engl. translation).

G. M. Kosolapoff

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TERENT'YEV, A.P.; KOST, A.N.; BERLIN, A.M.

Syntheses with the aid of acrylic acid nitrile. Part 22. New method for the synthesis of pyrrolines. Zhur. ob.khim. 25 no.8:1613-1616 Ag '55. (MLRA 9:2)

1.Moskovskiy gosudarstvennyy universitet.
(Pyrroline) (Nitriles)

KOST, A.N.; GRANDBERG, I.I.

Reduction by means of formic acid and of its derivatives. Part 1. Reduction of azines and hydrazones. Zhur.ob.khim. 25 no.9:1719-1723 S '55. (MIRA 9:2)

1.Moskovskiy gosudarstvennyy universitet.
(Reduction, Chemical) (Azines) (Hydrazones)

Kost A. N.

Chem

Reduction with formic acid and its derivatives. II. Reduction of quinoline. A. N. Kost and L. G. Yudin. *J. Gen. Chem. U.S.S.R.* 25, 1891-3(1955)(Engl. translation).—See *C.A.* 50, 804'h. B. M. R.

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Kost, A. N.

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Reduction with formic acid and its derivatives. II. Reduction of quinoline. A. N. Kost and L. G. Yudin (Moscow State Univ.). *Zhur. Obshchei Khim.* 25, 1047-50(1955); cf. *C.A.* 50, 4800*i*, 5544*e*.—Refluxing 12.9 g. quinoline, 23 g. 100% HCO_2H, and 34 g. HCO_2Na 21 hrs. with stirring, adding H_2O and excess 30% NaOH, extg. with Et_2O, and distg. the ext. gave 85% *N-formyl-1,2,3,4-tetrahydroquinoline* (I), b_3 145-7°, m. 38.5° (from Et_2O-petr. ether). I refluxed 1 hr. with concd. HCl gave 94.4% *1,2,3,4-tetrahydroquinoline*, b_{3-4} 95-7°, n_D^{20} 1.5951, d_{20} 1.0509; *HCl salt*, m. 180°; *PhNCO deriv.*, m. 98°; *Bz deriv.*, m. 74°; *picrate*, m. 140°. Quinoline (12.9 g.), 6.5 g. HCO_2NH_2, and 2.3 g. 100% HCO_2H refluxed, three 0.5-g. portions added at 1.5-hr. intervals (total reflux time 6 hrs.), the mixt. dild. with aq. NaOH and extd. with Et_2O, the ext. evapd., and the residue refluxed 20 min. with 10 g. 100% HCO_2H gave 55% I.

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Kost, A.N.

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Synthesis with acrylonitrile. XXI. Synthesis and properties of 1-indolepropionic acids. A. P. Terent'ev, A. N. Kost, and V. A. Smit (State Univ., Moscow). *Zhur. Obshchei Khim.* 25, 1959-66(1955); cf. C.A. 47, 12237*h*.—It was shown that the 2-cyanoethyl group can be cleaved from indole ring if it is located in 1-position; the mol. is stable if the group is in the 3-position. To a stirred mixt. of 11.7 g. indole, 10.6 g. CH_2:CHCN (Ia), and 50 ml. C_6H_6 was added 0.6 g. powd. KOH (exothermic reaction) and after 1-2 hrs. the mixt. was filtered and distd. yielding 95% *1-indolepropionitrile*, b_3 168-80°, m. 47°. Refluxed with 10% KOH 3 hrs. it gave 95% *1-indolepropionic acid* (I), m. 85-6° (crude), m. 90-1° (from aq. EtOH-HCl). Heating 11.7 g. indole, 8 g. ethylene cyanohydrin, and 6 g. solid KOH in 100 ml. 95% EtOH in autoclave 6 hrs. at 190-200° gave 62% I; NaOH gave a 41% yield; the best yield was 90% attained with KOH in 6 hrs. at 220°. Similar reaction using $EtOCH_2CH_2CN$ gave a 47% yield in 6 hrs. at 200°; in refluxing C_6H_6 only a 12% yield was obtained. The autoclave reaction as above of indole and $Me_2NCH_2CH_2CN$ with solid KOH in 95% EtOH gave 53% I; only 15% was obtained in refluxing xylene. Stirring 3.9 g. 2-methylindole, 3.4 g. Ia, 0.2 g. powd. KOH and 15 ml. C_6H_6 1 hr. at room temp. and 1 hr. at reflux gave 77% *2-methyl-1-indolepropionitrile*, m. 83°, b_7 170-80°; hydrolysis with KOH gave *2-methyl-1-indolepropionic acid*, m. 111-12°. Similar reaction of 34 g. 3-indolepropionitrile (II) and 21.2 g. Ia with powd. KOH in C_6H_6 gave 97% *1,3-indolebispropionitrile*, (III), m. 88-9° (crude), m. 96-7° (from EtOH); hydrolysis with 10% KOH gave the free *dicarboxylic acid*, m. 146° (from aq. EtOH). Similar condensation of 2-methyl-3-indolepropionitrile with Ia gave 93% *2-methyl-1,3-indolebispropionitrile*, m. 144-5° (from EtOH), which gave 100% of the *dicarboxylic acid*, m. 128° (from H_2O). Indole (5.8 g.), 10 g. $EtO_2CCH:CH_2$, and 0.3 g. powd. KOH stirred 1 hr. at room temp. in 25 ml. C_6H_6, then refluxed 2 hrs. gave 30% *Et 1-indolepropionate*, b_2 135-50°, which gave the free acid, m. 85-6°; this cleaves with superheated steam to indole. Similarly, 1,3-indolebispropionic acid with superheated steam at 280° gave 3-indolepropionic acid. Heating III with a little hydroquinone under N to 250° gave 92% II, m. 68°; refluxing I with 50% KOH 8 hrs. in NH_3 stream gave no indole and nearly all acid was recovered. However similar treatment of 1-indolepropionitrile gave about 10% indole and 80% I. **XXII. New method of synthesis of pyrrolines.** A. P. Terent'ev, A. N. Kost, and A. M. Berlin. *Ibid.* 1613-16.—To 91.2 g. iso-Pr_2CO and EtONa (0.6 g. Na in 10 ml. EtOH), heated on a steam bath, was added 21. g. CH_2:CHCN and, heated 4.5 hrs. longer, the mixt. after neutralization with H_2SO_4 gave 40% *γ-methyl-γ-isobutyrylvaleronitrile*, b_4 106-8°, b_7 116-18°, n_D^{20} 1.4132, d_{20} 0.9222; this (15 g.) in 300 ml. 3% H_2O_2 3 ml. 6*N* NaOH and EtOH to form a clear soln. was heated 6 hrs. at 50-60°, neutralized and evapd. yielding 89% *γ-methyl-γ-isobutyrylvaleramide* (I), m. 90° (from C_6H_6). Similarly cyanoethylation of isobutyrophenone gave *γ-methyl-γ-benzoylvaleronitrile*, $b_{0.5}$ 159-61°, n_D^{20} 1.5200, d_{20} 1.0469, which hydrolyzed as above to 93.5% *γ-methyl-γ-benzoylvaleramide* (II), m. 145° (from H_2O). To 23 g. NaOH in 300 ml. H_2O at −3° was added 5.5 ml. Br followed by 14.2 g. I and after 2 hrs. on a steam bath and addn. of NaOH there was isolated 70% *3,3-dimethyl-2-isopropyl-2-pyrroline*, b_{10} 157-8°, n_D^{20} 1.4471, d_{20} 0.8340, which causes headaches on inhalation and eye irritation; *picrate*, decomp. 189°; *styphnate*, m. 184°; *flavianate*, an oil; *N-benzenesulfonyl deriv.*, oil; *N-phenylcarbamide deriv.*, $C_{16}H_{22}N_2O$, m. 203°. Similarly II gave 58% *3,3-dimethyl-2-phenylpyrroline*, b_2 119-21°, n_D^{20} 1.5440, d_{20} 0.9983; *picrate*, m. 160°; *N-phenylcarbamide*, m. 230°.

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Kost A.N.

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Reactions of hydrazine derivatives. I. Synthesis of 1,1-pentamethylenebicyclo[0.1.4]heptane. A. N. Kost and I. I. Grandberg (State Univ., Moscow). *Zhur. Obshchei Khim.* 25, 2064-70(1955); cf. Zelinskii, *et al.*, *C.A.* 27, 2430.—To 166 g. cyclohexanone was added 52 g. 90% $N_2H_4.H_2O$ in 70 ml. H_2O at 70-80° and, after addn. of 100 ml. Et_2O, the mixt. was left overnight; after addn. of 100 ml. H_2O and 150 ml. Et_2O, the org. layer was sepd. and distd., yielding 93.7% *cyclohexanone azine*, b_{16} 142-6°, n_D^{20} 1.5202, m. 34°. This (90 g.) was treated with good stirring with 40.5 g. dry $(CO_2H)_2$ and heated 2 hrs. at 70-5° under CO_2; treatment of the cooled mass with an aq. soln. of 87 g. K_2CO_3 in 600 ml. H_2O and extn. with C_6H_6 gave on distn. under N 90.6% easily oxidizable *3,4-tetramethylene-5,5-pentamethylenepyrazoline* (I), b_{15} 165-7°, m. 00° (*phenylureido deriv.*, m. 122°). If, however, the azine (38.4 g.) were treated with 11.3 g. 100% HCO_2H and heated 3 hrs. at 40-50°, then treated with NH_4OH, and extd. with C_6H_6, there was obtained 20.6% I and 28.1 g. *N-formyl deriv.* of I, b_{15} 180-210°, m. 73°, which hydrolyzed with HCl in 1

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A. N. Kost

ln, at 105° to I. I (98 g.) and 2 g. LiOH heated on an air
bath with slow distn. gave, after purification of the result-
ing hydrocarbon with 40% and 30% HCO_2H, then with Na,
75.1% *1,1-pentamethylenebicyclo[0.1,4]heptane* (II), b_{744}
232-2.5°, n_D^{20} 1.4973; a very pure specimen b_{744} 232°, b_{22}
98°, n_D^{20} 1.4972, d_{20} 0.9278, f.p. about −73°. A 57.8%
yield is obtained (based on cyclohexanone) without iso-
lation of the above intermediates. II does not react with
BzO_2H; heated with S to 210° it gave 44.5% Ph_2. II with
HBr in AcOH at 0° gave *1-bromo-1-cyclohexylcyclohexane*, m.
39.5° (crude), m. 40° (from MeOH-Me_2CO); the bromide
heated with $PhNH_2$ in MePh gave 91.5% *1-cyclohexylcyclo-*
hexene, b_{744} 236°, n_D^{20} 1.4948, d_{20} 0.9012, which treated with
dry HCl in AcOH gave 100% *1-chloro-1-cyclohexylcyclohex-*
ane, m. 39.5°, also formed from II and HCl in AcOH; the
olefin with HBr gave the above bromide. II and aq.
$Hg(OAc)_2$ in 20 days at 5° gave a *solid*, decomp. 150-80°,
of unknown structure which contains Hg. II does not react
with H over Pt at 250°.

G. M. Kosolapoff

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Kost, A. N.

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Chem

Reduction with formic acid and its derivatives. III. Synthesis of substituted α-piperidones. A. N. Kost, T. A. Shchegoleva, and L. G. Yudin (State Univ., Moscow). *Zhur. Obshchei Khim.* 25, 2464-9(1955); cf. C.A. 50, 8044h. —Reactions of 53 g. $CH_2:CHCN$ and 260 g. $AcCH_2CO_2Et$ with EtONa in EtOH in 48 hrs. gave 50% *γ-carbethoxy-δ-oxocapronitrile*, b_4 143-4°, n_D^{20} 1.4462, which refluxed with aq. K_2CO_3 3.5 hrs. gave 70% *δ-oxocapronitrile*, b_2 108-9°, n_D^{20} 1.4403. This (10 g.) and 34 g. HCO_2Na refluxed with 23 g. 100% HCO_2H, cooled, and dild., then treated with excess 40% NaOH gave 68% *2-methyl-6-piperidone*, m. 85°, which refluxed 5 hrs. with concd. HCl gave *δ-aminocaproic acid.HCl*, m. 140-7°. A 24-hr. reaction of 20.5 g. $CH_2:CHCN$ with 178 g. MeEtCO in the presence of EtONa in EtOH gave 27-30% *γ-acetylvaleronitrile*, b_{11} 110-11°, n_D^{20} 1.4355, which (10 g.) refluxed 30 hrs. with 30.5 g. HCO_2Na and 20.8 g. HCO_2H similarly gave 74% *2,3-dimethyl-6-piperidone*, m. 99°. Dry MePrCO (109 g.) treated with 3 ml. 10% EtONa-EtOH, followed by 17.1 g. $CH_2:CHCN$ added over 1.5 hrs. and heating 6 hrs. on a steam bath, gave after neutralization with AcOH 20% *γ-acetylcapronitrile* (I), b_6 115-16°, n_D^{20} 1.4391, d_{20} 0.9024. To 30 g. $AcCHEtCO_2Et$ and 4 ml. 10% EtONa-EtOH was added at 10-12° in 15 min. 10 g. $CH_2:CHCN$; after 4 hrs. the soln. was acidified with AcOH and distd. yielding 71% *γ-acetyl-γ-carbethoxycapronitrile*, b_{11} 164-4.5°, n_D^{20} 1.4502, d_{20} 1.0518, which refluxed 4 hrs. with aq. Na_2CO_3 gave 21% I, b_{20} 142-3°. I (11 g.) refluxed 40 hrs. with 18.4 g. HCO_2H and 27.1 g. HCO_2Na then treated with 12.2 g. HCO_2H and refluxed 23 hrs., gave after usual treatment 50% *2-methyl-3-ethyl-6-piperidone*, b_{11} 152-5°.

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REDUCTION WITH FORMIC ACID

m. 40-3°. Similarly γ-methyl-γ-isobutyrylvaleronitrile gave 60% *3,3-dimethyl-2-isopropyl-6-piperidone*, m. 111-12°. Similarly 10 g. 2-(2-cyanoethyl)cyclohexanone refluxed 20 hrs. with 10.1 g. HCO_2H and 23.8 g. HCO_2Na gave 72% *trans-octahydro-α-quinolone*, m. 151°; no octahydro deriv. is formed with HCO_2H alone. Refluxing the product with concd. HCl 5 hrs. gave *β-(2-aminocyclohexyl)propionic acid-HCl*, m. 173-4°, from which was prepd. *trans-β-(2-benzamidocyclohexyl)propionic acid*, m. 200°, by action of BzCl. To 10 g. $BzCH_2CH_2CN$, 200 ml. 3% H_2O_2, and 2 ml. 6N NaOH was added enough EtOH to form a soln., which heated 5 hrs. at 50-60°, yielded after concn. and neutralization 45% $BzCH_2CH_2CONH_2$, m. 125°; a 30% yield resulted from keeping the nitrile in concd. H_2SO_4 2 hrs. The amide (5 g.) refluxed 40 hrs. with 10.2 g. HCO_2Na and 7 g. HCO_2H gave after cooling, removal of tar and addn. of concd. NaOH, a resinous mass which heated briefly with 1:1 HCl gave 30% *2-phenyl-6-pyrrolidone*, m. 108°; this refluxed 10 hrs. with concd. HCl gave *γ-amino-γ-phenylbutyric acid-HCl*, m. 179°. Benzoylpropionitrile under the above conditions gives but a very poor yield of the phenylpyrrolidone owing to formation of much tar. Heating β-benzoylpropionitrile with $HCONH_2$ and a little HCO_2NH_4 6 hrs. at 160° gave a red solid, decomp. 250°. G. M. K.

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KOST, A.N.

KOST, A.N.; YUDIN, L.G.: SHIPOV, A.E.

Reduction by formic acid and its derivatives. Part 4: Reduction of N-alkylpyridinium salts. Vest.Mosk.un. Ser.mat.,mekh.,astron., fiz.,khim. 11 no.1:209-212 '56. (MIRA 10:12)

1. Kafedra organicheskoy khimii Moskovskogo universiteta.
(Reduction, Chemical) (Pyridinium compounds)

Abstract: The ultraviolet absorption spectra of CH_3OH solutions of the following compounds were studied: a) acetaldehyde, butyl-, isobutyl- and isovaleraldehyde azines; b) azines of acetone (I), methylethylketone, methylpropylketone, cyclohexanone [illegible] (III); c) substituted pyrazolines and their hydrochlorides: 5-CH_3-, 1-CHO-5-CH_3-, 4-CH_3-5-C_2H_5-, 4-iso-C_3H_7-5-iso-C_4H_9-, 4,4-$(CH_3)_2$-5-iso-C_3H_7-, 1-CHO-4,4-$(CH_3)_2$-5-iso-C_3H_7-, 1-CH_3CO-4,4-$(CH_3)_2$-5-iso-C_3H_7-, 1.4,4-

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under 225 m was confirmed; it was found that ketones,
exception of III, absorb in the range of about 230 mμ (III
absorbs at 230 mμ). It was established that the majority of
the studied pyrazolines have 2 absorption bands: 225 to 230 (log =
3 to 5) and 320 to 330 mμ (log ε = 1 to 2) and that the charac-
ter of the absorption curves depends little on the substitutes;
the spectrum change at the transition to hydrochlorides is little
characteristic. Cyclopentylidenecyclopentanone (V) was synthe-
tized by the reaction of 197 g of cyclopentanone and 96 g of
CaC_2 (two hour's boiling), yield 54%, boiling point 119 to 122°
at 14 mm, 136 to 137° at 25 mm, d_4^{20} = 1.0169, $n^{20}D$ = 1.5209.

Card : 2/3

TERENT'YEV, A.P.; KOST, A.N.; SMIT, V.A.

Synthesis with the aid of acrylic acid nitrile. Part 25. Cyanoethylation of indole. Zhur.ob.khim. 26 no.2:557-559 F '56. (MLRA 9:8)

1. Moskovskiy gosudarstvennyy universitet.
(Cyanoethylation) (Indole) (Acrylonitrile)

Kost, A.N.

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Reactions of hydrazine derivatives. II. Synthesis of 1,2,3,4,5,6,7,8-octahydrocarbazole. A. N. Kost and I. I. Grandberg (State Univ., Moscow). *Zhur. Obshchei Khim.* 26, 565-8(1956); cf. C.A. 50, 8009*b*.—Heating 44.2 g. freshly distd. cyclohexanone azine (I), 6 g. glass wool and 0.15 g. $ZnCl_2$ 4 hrs. at 210-30°, followed by distn. *in vacuo* gave 79.3% *1,2,3,4,5,6,7,8-octahydrocarbazole*, b_3 161.6-2.5°, m. 96°, which oxidizes rapidly in air; it is storable in ampuls under NH_3. To 19.2 g. I in 50 ml. dry dioxane was added 11.8 g. AcCl; after refluxing 0.5 hr. and quenching in H_2O there formed 82.5% *N-acetyloctahydrocarbazole*, m. 71°, which can be stored in air. I heated with $HCONH_2$ 3 hrs. at 160-90° gave 37.4% *N-formyl-3,4-tetramethylene-5,5-pentamethylenepyrazoline*, m. 74°, b_4 144-203° (crude), which with hot concd. HCl gave *3,4-tetramethylene-5,5-pentamethylenepyrazoline* (II), m. 63°. I and $PhNH_2.HCl$ heated to 120-40° gave a vigorous reaction which gave some octahydrocarbazole, $PhNH_2$, and much II, b_{11} 161-9° (*N-phenylcarbamide deriv.*, m. 122°; if the reaction is run at 210-30° 3 hrs. 10.7% octahydrocarbazole is formed along with 61% cyclohexylcyclohexene). Quinoline-HCl gave in a similar reaction 40% octahydrocarbazole and 44.6% cyclohexylcyclohexene. I heated 2.5 hrs. at 210-30° with acid aluminosilicate catalyst gave 39% cyclohexylcyclohexene. Addn. of 19.2 g. I in MeOH to 13.65 g. $ZnCl_2$ gave a solid, m. 230-40° (decompn.), containing 7-10% N; the same formed in aq. MeOH medium. This solid complex is converted to tar with acids, while bases regenerate I; heating the complex to 250-60° does not yield

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octahydrocarbazole. I and Cu_2Cl_2 in MeOH yield a complex $C_{12}H_{16}N_2 \cdot CuCl$, which is unstable. To 16.1 g. II at reflux was added NH_2[illegible] for 3 hrs. yielding 50.7% *1,1-pentamethylenebicyclo[0.1.4]heptane* (III), b_{760} 231-2°, n_D^{20} 1.4970; this purified with hot Cu acetate soln., steam distn., treatment with BzOOH, Na_2CO_3, and $KMnO_4$ gave the pure substance, b_{760} 230.1°, n_D^{20} 1.4900, d_{20} 0.9020. II and $ZnCl_2$ similarly gave a mixture of the bicyclo compound and cyclohexylcyclohexene. III heated with $PhNH_2 \cdot HCl$ 5 hrs. at reflux gave 95.4% [illegible]-cyclohexylcyclohexene, b_{760} [illegible]7-7.8°, n_D^{20} 1.4940, d_{20} 0.9069. III heated with $ZnCl_2$ gave tars and unidentified hydrocarbons. III. 3-Arylpyrazolines. A. N. Kost and V. V. Ershov. *Vestnik Moskov. Univ.* 10, No. 12, Ser. *Fiz.-Mat. i Estestven. Nauk* No. 8, 115-17(1955).—Refluxing 0.5 mole ketone, 0.5 mole $Et_2NH \cdot HCl$, 18 g. paraform, and 40 ml. EtOH 4-6 hrs. (1 ml. HCl added in refractory cases), the soln. dild. with 1 vol. H_2O, washed with Et_2O, made alk. with NaOH and extd. with Et_2O gave on passage of dry HCl into the ext. the following *HCl salts*: *p-$MeC_6H_4COCH_2CH_2NEt_2$*, m. 110°, 60%; *p-$MeOC_6H_4COCH_2CH_2NEt_2$*, m. 119°, 73.0%; *p-iso-$PrC_6H_4COCH_2CH_2NEt_2$*, m. 138°, 64.7%. To 8 ml. 40% NaOH, 18 ml. $N_2H_4 \cdot H_2O$, and 50 ml. MeOH was added in 15-20 min. 10 g. diethylaminopropiophenone-HCl in 50 ml. MeOH; the soln. refluxed 3 hrs. and evapd. gave 83% *3-phenylpyrazoline*, b_1 130°, m. 44°; *N-nitroso deriv.*, m. 151-3°. Similar procedure gave 93% *3-p-tolylpyrazoline*, m. 77-80° (*N-nitroso deriv.*, m. 130°) if the Mannich salt is

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added at once there is formed some 1-p-tolyl-3-(3-p-tolyl-1-
pyrazolyl)-1-propanone hydrazone, m. 126-7°); 86% 3,5-
methoxyphenylpyrazoline, m. 91-9° (N-nitroso deriv., m.
100°); 1-p-methoxyphenyl-3-(3-p-methoxyphenyl-1-pyrazolyl)-
1-propanone hydrazone, m. 101-1°; 3-p-isopropylphenyl-
pyrazoline, b_1 131° (N-nitroso deriv., m. 130-7°); 1-p-iso-
propylphenyl-3-(3-p-isopropylphenyl-1-pyrazolyl)-1-propa-
none hydrazone, m. 100°). New synthesis of benzyl-
hydrazine. I. I. Grandberg and A. N. Kost. *Ibid.* 11-
20.—EtOAc (204 g.) was added dropwise to a boiling soln. of
150 g. 85% $N_2H_4.H_2O$ and 50 ml. EtOH over 3 hrs. After
refluxing 8 hrs. the EtOH was removed *in vacuo*, the residual
acetylhydrazine added to 500 ml. Me_2CO, the mixt. chilled
after 5 hrs., the ppt. filtered off and washed with Et_2O, and
the combined filtrates evapd. yielding more product.
Total yield of *isopropylideneacetylhydrazine*, m. 135°, was
78%. This (171 g.) in 800 ml. Me_2CO was treated with
stirring and cooling with 60 g. NaOH in 60 ml. H_2O, and
stirred 2 hrs. yielding a ppt. (10 %) of *$Me_2C:NN:CMeONa$*,
which was dried at 75-80°. This (32.6 g.) was refluxed 40
min. with 80 ml. abs. xylene and 25.3 g. $PhCH_2Cl$, NaCl
filtered off and the soln. evapd. to 180 ml. The residue,
dried 4 hrs. at 80°, was taken up in 100 ml. abs. EtOH and
the undissolved $N_2H_4.HCl$ sepd., the filtrate evapd. to 50
ml. and dild. with 250 ml. [illegible] yielded 75.0% *benzyl-
hydrazine mono-HCl salt*, m. 1 .5° (from abs. EtOH).
Nitrosation gave the *nitroso deriv.*, m. 71.5°; BzCl gave the
dibenzoyl deriv., m. 148-9°. Cf. Wieland and Schamberg,
C.A. 15, 71.

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Synthesis with acrylic acid nitrile. XXVI. Synthesis of some β-alkoxypropionamides. A. P. Terent'ev, A. N. Kost, and A. M. Berlin (*Zh. obshch. Khim.*, 1956, 26, 719—723).—Acrylonitrile when reacted with BuOH led to β-butoxypropionitrile which, after heating in aq. alkali or HCl was converted to β-butoxypropionic acid (I) (with partial decomposition to BuOH). Hydrolysis at room temp. with H_2SO_4 gave amides (20% yields), as did 3% H_2O_2 in dil. alkali. Best results were obtained with 0·2—0·3% aq. NaOH and alcohol. Synthesis of amides after cyanoethylation, via the acid and chloroanhydride, was also investigated. In this way β-methoxy-, β-ethoxy- and β-butoxy-propionitriles were obtained; β-cyanoethyl ethers (II) of β-butoxyethanol gave amides in very good yields. ββ'-dicyanodiethyl esters of ethylene glycol gave diamides with good yields. The synthesis of II was by cyanoethylation of β-butoxyethanol in presence of 2% aq. KOH. (Neutralization is necessary in synthesis of such high-boiling β-alkoxypropionitriles.) Amides obtained crystallized slowly and were sol. in water. By Hofmann re-arrangement β-butoxyethylamine was obtained, which easily converted to I by hydrolysis. A. L. B.

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USSR/Organic Chemistry. Synthetic Organic Chemistry. E-2

Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19206.

Author : Kost A. N., Grandberg I. I.
Inst :
Title : Reactions of Hydrazine Derivatives. V. Synthesis of 3, 5,5-trialkylpyrazolenes.

Orig Pub: Zh. obshch. khimiyi, 1956, 26, No 6, 1717-1720.

Abstract: With the intention of widening the possibilities of the synthesis of 3,5,5-trialkylpyrazolenes (TAP) the regrouping of azines of asymmetrical ketones, obtained from the hydrazone hydrate of cyclohexanone (I) by the action of anhydrous HCOOH and $(COOH)_2$ is investigated. With the help of the synthesis of 5-methyl-3,5-diethylprazolene (II) by isomerization of the azine of methylethylketone (III), and the action of 96% hydrazinohydrate (IV) on 3-methylhepton-3-one-5 (V), the assumption of Curtius

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mixed azine of acetone and VI (VII) is obtained by the addition of acetone (VIII) in drops at 50° to II (left standing 4 hours at 50-55° and adding potassium carbonate and ether). Yield of VII 59.5%, b.p. 96-97°/8-9 mm,

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Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19206.

n20D 1.4938, d_4^{20}0.9279. Simultaneously are obtained 16 g. of azine of acetone (IX) and 21 g. of azine VI. From 2 moles methylethylketone (X) and 1 mole IV (100°, 2 hours) is synthesized III, yield 89.5%, b.p. 108-110°/125 mm. Analogically are obtained IX, yield 80%, b.p. 129-132/753 mm, n20D 1.4533, d_4^{20}0.8434, and azine of methylpropylketone (XI) (100, 6 hours), yield 79.8%, b.p. 97°/22 mm, 100°/25 mm, 130°/81 mm, n20D 1.4565, d_4^{20}0.8401. 3,3,5-trimethylpyrazolene (XII) is obtained by the addition in drops of 1 mole of IX to 1.1 mole of anhydrous $(HOOC)_2$ and by heating (100°, 4 hours). Oxalate XII is decomposed with a surplus of 40% solution of KOH; the yield is XII 78%, b.p. 52.5°/15 mm, n20D 1.4573, d_4^{20}0.9025. 3-methyl-5,5-pentamethylenepyrazolene (XIII) is synthesized analogically from 60 g VII, yield 50% b.p. 125-132°/21-22 mm, n20D 1.4975, d_4^{20}0.9830. The acetyl derivative is XIII, m.p. 86°

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Reduction by formic acid and derivatives. V. Reduction of quinoline salts. A. N. Kost and L. G. Yudin (Zhur. Obshchei Khim., 1956, 26, 1720–1723).—Satisfactory reduction of quinoline to N-formyl-1 : 2 : 3 : 4-tetrahydroquinoline is obtained by heating with formic acid (I) or with I and sodium formate (II) and similarly in the case of quinoline salts. Thus by using 5 mol. of sodium formate and 8 mol. of formic acid per mol. of quinoline salts, the N-alkyl-1 : 2 : 3 : 4-tetrahydroquinoline (III) yield attained 80—85%. Thoroughly pure I, with or without II, gave negligible yields however. Reactions demand protracted heating, during which there is some resin formation. By substituting triethylamine for sodium formate, substantially higher yields (~93%) of III were obtained and reaction time was reduced from 10 hr. to 3—5 hr.; resin formation was also avoided. Triethylamine added to the inorg. formate mixtures had little effect. The use of 2 mol. triethylamine per mol. quinoline salt gave the best results.

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butyl-(VIII)-3,5,5-trimethylpyrazolines. Structure VI
is determined by a counter synthesis according to Kizhner
from mezityloxide and hydrazine hydrate; structure IX--
from ...ization of I is also accom-
benzylation

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Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19207

plished by heating (2 hours, 100°) with the hydrochloride
VI (VIa). To 11.2 g. of I is gradually added an equi-
molecular amount II, the mixture is left standing 1-2
hours at 20° and 5.2 g. hydrobromide VI, m.p. 170° (from
alc.) is separated; the rest is heated 1 hour at 100°
boiled 2-3 hours with 100-150 cc 2N HCl, and alkalized
and extracted with ether VI, yield 2 g., b.p. 65-69/19 mm,
$n^{20}D$ 1.4571; picrate, m.p. 134.5 and VII, yield 18%, b.p.
77-80°/19, mm, $n^{20}D$ 1.4676, d_4^{20} 0.8957; picrate, m.p.
86-87° (from alc.). Analogically from III is obtained
VIa, yield 1 g. m.p. 171-172° (from alc.); VI, general
yield 51%, and VII, yield 19%; from 22.4 g. I and 27.5
g. IV (heating 46 hours at 90-100°)--VI (traces.) and
VIII, yield 38.7%, b.p. 70°/6 mm $n^{20}D$ 1.4551. d_4^{20}
g. I and 13.6 g. V(heating 2 hours at

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Reduction with formic acid and its derivatives. II. Synthesis of N-cycloalkylethanolamines. A. N. Kost and N. I. Stupnikova (State Univ., Moscow). Zhur. Obshchei Khim. 26, 2485-7(1956); cf. C.A. 51, 1958e; U.S. 2,361,245, C.A. 35, 6973^9.—Slow distn. of H_2O from 31 g. $HOCH_2CH_2NH_2$ and 100 ml. 85% HCO_2H up to pot temp. 200°, followed by cooling to 100°, addn. of 2 g. Raney Ni and 29.4 g. cyclohexanone and refluxing 3 hrs. while adding 30 g. 85% HCO_2H followed by sepn. of Ni, refluxing the soln. 6 hrs. with 10% HCl, addn. of NaOH, and extn. with Et_2O gave 94% *N-cyclohexylethanolamine*, b_1 118-19°, m. 42°; *picrate*, m. 129°; *dinitro-o-cresolate*, m. 101°. In a similar reaction 2-methylcyclohexanone gave 77% *N-(2-methylcyclohexyl)ethanolamine*, b_1 114-15°, b_2 117-18°, n_D^{20} 1.4830, d_{20} 0.9719; *picrate*, m. 114°. 3-Methylcyclohexanone gave 78% *N-(3-methylcyclohexyl)ethanolamine*, b_{12} 110-25°, b_1 111-19°, n_D^{20} 1.4779, d_{20} 0.9600; *picrate*, m. 85°. 4-Methylcyclohexanone gave 77% *N-(4-methylcyclohexyl)ethanolamine*, b_4 120°, n_D^{20} 1.4774, d_{20} 0.9547; *picrate*, m. 109°. Cyclopentanone gave 67.7% *N-cyclopentylethanolamine*, b_{12} 114.5-[illegible]°, n_D^{20} 1.4828, d_{20} 0.9942; *picrate*, m. 119°. G. M. Kosolapoff

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KOST, A.N.; GRANDBERG, I.I.; GOLUBEVA, G.A.

Reactions of hydrazine derivatives. Part 8. Cyclization of aldazines by alkyl halides. Zhur.ob.khim. 26 no.9:2604-2607 S '56. (MLRA 9:11)

1. Moskovskiy gosudarstvennyy universitet.
(Azines) (Cyclization) (Alkyl halides)

Kost, A.N.

TERENT'YEV, A.P.; KOST, A.N.; SALTYKOVA, Yu.V.; YERSHOV, V.V.

Synthesis with help of acrylic acid nitril. Part 29: Cyanoethylation of some ketones. Zhur. ob. khim. 26 no.10:2925-2928 O '56.
(MIRA 11:3)

1. Moskovskiy Gosudarstvennyy universitet.
(Ethylation) (Ketones)

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Reactions of hydrazine derivatives. IX. Reaction of phenylhydrazine with substituted propionitriles. A. N. Kost and V. V. Ershov (State Univ., Moscow). Zhur. Obshchei Khim. 26, 3123-4(1956); cf. C.A. 48, 2669i; 51, 5054f.—EtOH (20 ml.) contg. 0.5 g. Na treated with 10.8 g. PhNHNH$_2$ and 0.1 mole RCH$_2$CH$_2$CN and refluxed 5 hrs. gave on cooling a ppt. of 3-amino-1-phenyl-2-pyrazoline (I), m. 169°. The % yields for various R(CH$_2$)$_2$CN (R shown) were as follows: Cl 58.5, HO (in EtOH) 37.2, (in BuOH) 19.3%; EtO (in EtOH) 83.3, (in BuOH) 87.7; BuO (in EtOH) 88.2, (in BuOH) 82.8; Me$_2$N (in EtOH) (14 hrs. reaction) 22.5, (in BuOH, 5.5 hrs.) 87%; Et$_2$N (in BuOH) (8 hrs.) 22.4. I with Ac$_2$O gave the 3-AcNH analog, m. 109°, absorption max. in MeOH at 252.5 and 293 mμ. I refluxed 1 hr. with p-HOC$_6$H$_4$CHO in EtOH gave 80% 3-p-HOC$_6$H$_4$CH:N analog, decomp. 128°, absorption max. in MeOH at 262 and 432 mμ, readily yielding with Cu^{++} salts a brown *Cu complex*, m. 145° (decompn.). X. Absorption spectra of azines and pyrazolines. N. B. Kupletskaya, A. N. Kost, and I. I. Grandberg. *Ibid.* 3125-8.—The absorption spectra of aldazines and ketazines derived from AcH, PrCHO, iso-PrCHO, iso-BuCHO, MeEtCO, MeCOPr, Me$_2$CO, and (CH$_2$)$_5$CO were shown; the aldazines had a max. below 225 mμ, while ketazines had a max. at about 230. Pyrazolines derived from the azines were also examd. The following absorption max. were

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found for the bases and their HCl salts, resp. (substituents on *pyrazoline* indicated): *5-Me*, 326 mμ, 310; *5,5-Me(OHC)*, 317, —; *4,5-MeEt*, 232 and 330, 227 and 327; *4,5-iso-Pr(iso-Bu)*, 231 and 331, 228, and 333; *4,4,5-Me₂(iso-Pr)*, 234, 281; *4,4,5,1-Me₂(iso-Pr)(OHC)* 236, —; *1,4,4,5-AcMe₂(iso-Pr)*, 242, —; *1,4,4,5-Me₃(iso-Pr)* 232, —; *5,3,5,1-MePr₂(OHC)* 233, —; *3-methyl-5,5-pentamethylene*, 228 and 333, 243; *3,4-tetramethylene-5,5-pentamethylene*, 231, 274; *1-formyl-3,4-tetramethylene-5,5-pentamethylene*, 237 —; *3,4-trimethylene-5,5-pentamethylene*, 324, 323 mμ. The latter was prepd. by heating 197 g. cyclopentanone in a Soxhlet app. with 96 g. CaC_2 3 hrs., yielding 84% *2-cyclopentylidenecyclopentanone*, b₁ 119-22°, b₁₁ 136-7°, n_D^{20} 1.5211, d_{20} 1.0169, which with N_2H_4 gave the corresponding *hydrazone*, m. 90-1°, stable if moistened with EtOH but decomps. rapidly in dry state. Refluxing 30 g. of the ketone in 15 ml. BuOH with 11.4 g. 96% $N_2H_4.H_2O$ 6 hrs. gave 95.7% *3,4-trimethylene-5,5-pentamethylenepyrazoline*, b_{12} 143°, n_D^{20} 1.5024, d_{20} 1.0049; the *picrate* and *nitroso* derivs. failed to crystallize. This pyrazoline also formed in 88% yield on refluxing the hydrazone in BuOH, b_{10-11} 140-5°, n_D^{20} 1.5017, d_{20} 1.0062. G. M. Kosolapoff

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KOST, D.N.,

)KUPLETSKAYA, N.B.; KOST, A.N.; GRANDBERG, I.I.

Reactions of hydrazine derivatives. Part 10. Absorption spectra of azines and pyrazolines. Zhur.ob.khim.26 no.11:3135-3138 N '56.
(MIRA 10:1)

1. Moskovskiy Gosudarstvennyy universitet.
(Pyridine--Spectra) (Pyrazoline--Spectra)